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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;  
im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
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**R C van Dijk**



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If no title is shown please refer to the description.  
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Symmetrical Triazine derivatives

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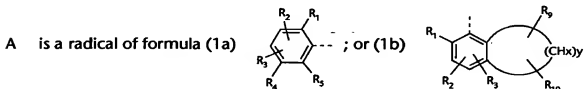
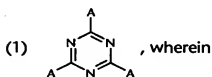
Symmetrical Triazine derivatives

The present invention relates to the use of specific symmetrical triazine derivatives for the protection of human and animal hair and skin against the damaging effect of UV radiation, cosmetic compositions comprising these triazine derivatives and process for preparation of these compounds.

Triazines which are symmetrically substituted by biphenyl or naphthyl are known, for example from US-A-6,225,467. they are used as for electroluminescent devices.

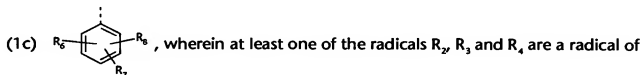
Surprisingly it has been found that these compounds can be used as highly effective UV absorbers for cosmetic applications.

Therefore, the present invention refers to the non-therapeutic use of the compounds of formula



R<sub>1</sub> and R<sub>3</sub> independently from each other are hydrogen; C<sub>1</sub>-C<sub>18</sub>alkyl; or C<sub>6</sub>-C<sub>12</sub>aryl;

R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently from each other are hydrogen; or a radical of formula



formula (1c);

R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> independently from each other are hydrogen; hydroxy; halogen; C<sub>1</sub>-C<sub>18</sub>alkyl; C<sub>1</sub>-C<sub>18</sub>alkoxy; C<sub>6</sub>-C<sub>12</sub>aryl; C<sub>6</sub>-C<sub>12</sub>aryloxy; C<sub>1</sub>-C<sub>18</sub>alkylthio; carboxy; -COOM; C<sub>1</sub>-C<sub>18</sub>alkylcarboxyl; aminocarbonyl; or mono- or di-C<sub>1</sub>-C<sub>18</sub>alkylamino; C<sub>1</sub>-C<sub>18</sub>acylamino; -COOH;

M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

C<sub>1</sub>-C<sub>18</sub>alkyl according to the definition for the radicals of the compound of formula (1) are straight-chain or branched alkyl radicals like methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.butyl, tert.butyl, amyl, isoamyl or tert.amyl, hexyl, 2-ethylhexyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl

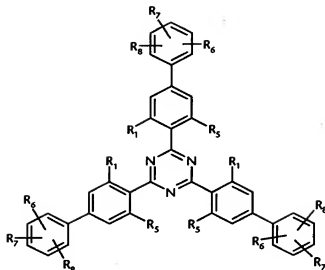
C<sub>1</sub>-C<sub>18</sub>alkyl according to the definition for the radicals of the compound of formula (1) may be substituted by methoxyethyl, ethoxypropyl, 2-ethylhexyl, hydroxyethyl, chloropropyl, N,N-diethylaminopropyl, cyanoethyl, phenethyl, benzyl, p-tert-butylphenethyl, p-tert-octylphenoxyethyl, 3-(2,4-di-tert-amylphenoxy)-propyl, ethoxycarbonylmethyl-2-(2-hydroxyethoxy)ethyl, or 2-furylethyl.

C<sub>1</sub>-C<sub>18</sub>alkyl according to the definition for the radicals of the compound of formula (1) are for example methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.butoxy, tert.butoxy, amyloxy, isoamyloxy or tert.amyloxy, hexyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy or octadecyloxy.

C<sub>6</sub>-C<sub>10</sub>aryl according to the definition for the radicals of the compound of formula (1) is for example naphthyl und preferably phenyl.

Preferably compounds of formula

(2)



are used, wherein

$R_1$ ,  $R_5$ ,  $R_7$ , and  $R_8$  are defined as in formula (1).

In formula (2)  $R_1$  and  $R_5$  are preferably hydrogen.

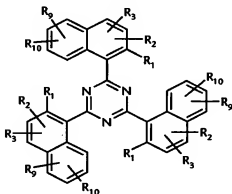
Most preferably compounds of formula (1) or (2) are used wherein  $R_7$  and  $R_8$  are hydrogen.

Compounds of formula (1) of preferred interest are those, wherein

$R_7$  is hydrogen; hydroxy;  $C_1$ - $C_3$ alkyl;  $C_1$ - $C_3$ alkoxy;  $-COOM$ ;  $-COOH$ ; or  $COOR_{10}$ ; and  $R_{10}$  is  $C_1$ - $C_3$ alkyl.

Furthermore compounds of formula

(3)



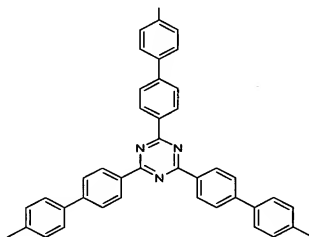
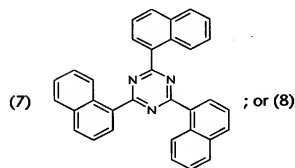
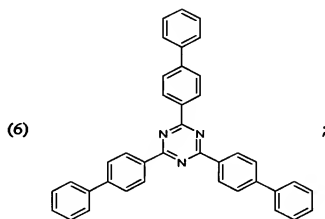
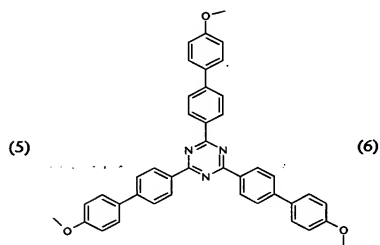
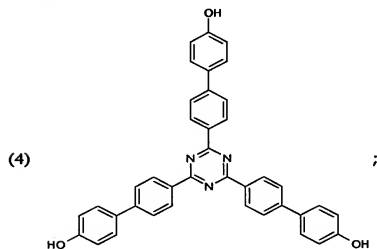
are preferably used, wherein

$R_1$ ,  $R_2$ ,  $R_3$ , and  $R_{10}$  are defined as in formula (1).

Preferably compounds of formula (3) are used, wherein

$R_{17}$ ,  $R_{27}$ ,  $R_{37}$ ,  $R_8$ , and  $R_{10}$  are hydrogen; or  $C_1$ - $C_{18}$ alkyl.

Examples of triazine derivatives, which are preferably used in the present invention are the compounds of formula



The compounds of the formula (1) according to the present invention are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular the skin and hair of humans and animals, from the harmful effects of UV radiation. These compounds are therefore suitable as sunscreens in cosmetic, pharmaceutical and veterinary medical preparations. These compounds can be used both in dissolved form and in the micronized state.

The UV absorbers according to the present invention – depending on the substituents of the triazine phenyl groups ( $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  in formula (1)) - can be used either in the dissolved state (soluble organic filters, solubilized organic filters) or in the micronised state (nanoscalar organic filters, particulate organic filters, UV-absorber pigments).

The triazine derivatives of formula (1) which have no alkyl substituents or only lower-alkyl substituents are characterized by a poor oil-solubility and a high melting point. They are therefore suitable particular UV absorbers in the micronized state.

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example:

- wet-milling (low viscous micronisation process for pumpable dispersions), with a hard grinding medium, for example zirconium silicate balls in a ball mill and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- wet-kneading (high viscous micronisation process non pump-able pastes) using a continuous or discontinuous (batch) kneader. For a wet-kneading process a solvent (water or cosmetically acceptable oils), a grinding-aid (surfactant, emulsifier) and a polymeric grinding aid may be used.
- Both processes may be used respectively
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc..
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g.  $CO_2$ ) in which the UV filter or filters is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;

- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As milling apparatus for the preparation of the micronised organic UV absorbers there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. Even more preferably mills are modern ball mills, manufactures of these mill-types are for example Netzsch (LMZ-mill), Drais (DCP-viscoflow or cosmo), Bühler AG (centrifugal mills) or Bachhofer. The grinding is preferably carried out with a grinding aid. As kneading apparatus for the preparation of the micronised organic UV absorbers examples are typical sigma-hook batch kneaders but also serial batch kneaders (IKA-Werke) or continuous kneaders (Contiuna from Werner und Pfeleiderer).

Useful low molecular weight grinding aids for all the above micronizing processes are surfactants and emulsifiers as disclosed below in the chapters "emulsifiers" and "surfactants" and "fatty alcohols"..

Useful polymeric grinding aids for water dispersion are cosmetically acceptable water soluble Polymers with  $M_n > 500$  g/mol for example: Acrylates (Salcare types), modified or non-modified polysaccharides, polyglucosides or xanthan gum. Furthermore an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, cetareth-25 or a phospholipid may be used. Oil dispersions may contain cosmetically acceptable waxy polymers or natural waxes as polymeric grinding aid to adjust viscosity during and after processing. Examples of other useful polymeric grinding aids are disclosed below in the chapter "polymers".

Useful solvents are water, brine, (poly-)ethylenglycol, glycerine or cosmetically acceptable oils. Other useful solvents are disclosed below in the chapters "esters of fatty acids", "natural and synthetic triglycerides including glyceryl esters and derivatives", "perlescent waxes", "hydrocarbon oils" and "silicones or siloxanes".

The micronised UV absorbers so obtained usually have an average particle size from 0.02 to 2 micrometer, preferably from 0.03 to 1.5 micrometer and more especially from 0.05 to 1.0 micrometer.



The UV absorbers according to the present invention can also be used dry in powder form. For that purpose the UV absorbers are subjected to known grinding methods, such as vacuum atomization, countercurrent spray-drying etc.. Such powders have a particle size of from 0.1 micrometer to 2 micrometer. To avoid the occurrence of agglomeration, the UV absorbers can be coated with a surface-active compound prior to the pulverization process, for example with an anionic, non-ionic or amphoteric surfactant, e.g. a phospholipid or a known polymer, such as PVP, an acrylate etc.

The UV absorbers according to the present invention can also be used in specific carriers for cosmetics, for example in solid lipid nanoparticles (SLN) or in inert sol-gel microcapsules wherein the UV absorbers are encapsulated.

The cosmetic formulations or pharmaceutical compositions according to the present invention can also contain one or more than one further UV filter as described in table 1-3.

The cosmetic or pharmaceutical preparations can be prepared by physically mixing the UV absorber(s) with the adjuvant using customary methods, for example by simply stirring together the individual components, especially by making use of the dissolution properties of already known cosmetic UV absorbers, for example octyl methoxy cinnamate, salicylic acid isooctyl ester, etc. The UV absorber can be used, for example, without further treatment, or in the micronised state, or in the form of a powder.

Cosmetic or pharmaceutical preparations contain from 0.05-40% by weight, based on the total weight of the composition, of one UV absorber or UV absorber mixtures.

Preference is given to the use of mixing ratios of the UV absorber of formula (1) according to the present invention and optionally further light-protective agents (as described in table 1-3) from 1:99 to 99:1, especially from 1:95 to 95:1 and preferably from 10:90 to 90:10, based on weight. Of special interest are mixing ratios of from 20:80 to 80:20, especially from 40:60 to 60:40 and preferably approximately 50:50. Such mixtures can be used, *inter alia*, to improve solubility or increase UV absorption.

The UV absorbers of formula (1) according to the present invention or combinations of UV filters are useful to protect skin, hair and/or natural or artificial hair color.

**Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;
benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzofuran-2-yl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2-(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl]-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis[[4-(tris(trimethylsilyloxy-silylpropyloxy)-2-hydroxy)-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2'-methylpropenyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2'-methyl-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-[4-ethylcarboxy]-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
2-phenylbenzimidazole-5-sulfonic acid and salts thereof;
menthyl o-aminobenzoates;
physical sunscreens coated or not as titanium dioxide, zinc oxide, iron oxides, mica, MnO, Fe <sub>2</sub> O <sub>3</sub> , Ce <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , (surface coatings: polymethylmethacrylate, methicone

(methylhydrogenpolysiloxane as described in CAS 9004-73-3), dimethicone, isopropyl titanium trisostearate (as described in CAS 61417-49-0), metal soaps as magnesium stearate (as described in CAS 4086-70-8), perfluoroalcohol phosphate as C9-15 fluoroalcohol phosphate (as described in CAS 74499-44-8; JP 5-86984, JP 4-330007)). The primary particle size is an average of 15nm-35nm and the particle size in dispersion is in the range of 100nm - 300nm.

aminohydroxy-benzophenone derivatives disclosed in DE 10011317, EP 1133980 and EP 1046391

phenyl-benzimidazole derivatives as disclosed in EP 1167358

the UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A. Shaath, Marcel Dekker, Inc., New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

Table 2. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention

(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

The generic scope of the UV absorbers is described in the left-hand column; specific compounds are indicated in the right-hand column

DE 100331804	Tab 1 p 4, tab 2 + 3 p 5
EP 613893	Ex 1-5 + 15, T 1, pp 6-8
EP 1000950	Comp. in table 1, pp 18-21
EP 1005855	T 3, p 13
EP 1008586	Ex 1-3, pp 13-15
EP 1008593	Ex 1-8, pp 4-5
EP 1027883	Compound VII, p 3
EP 1027883	Comp I-VI, p 3
EP 1028120	Ex 1-5, pp 5-13
EP 1059082	Ex 1; T 1, pp 9-11
EP 1060734	T 1-3, pp 11-14
EP 1064922	Compounds 1-34, pp 6-14
EP 1081140	Ex 1-9, pp 11-16
EP 1103549	Compounds 1-76, pp 39-51
EP 1108712	4,5-Dimorpholino-3-hydroxypyridazine
EP 1123934	T 3, p 10
EP 1129695	Ex 1-7, pp 13-14
EP 1167359	Ex 1 p11 and ex 2 p 12

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The generic scope of the UV absorbers is described in the left-hand column; specific compounds are indicated in the right-hand column

EP 1258481	Ex 1, pp 7,8
EP 420707 B1	Ex 3, p 13 (CAS Regno 80142-49-0)
EP 503338	T 1, pp 9-10
EP 517103	Ex 3,4,9,10 pp 6-7
EP 517104	Ex 1, T 1, pp 4-5; Ex 8, T 2, pp 6-8
EP 626950	all compounds
EP 669323	Ex 1-3, p 5
EP 780382	Ex 1-11, pp 5-7
EP 823418	Ex 1-4, pp 7-8
EP 826361	T 1, pp 5-6
EP 832641	Ex 5+6 p 7; t 2, p 8
EP 832642	Ex 22, T 3 pp, 10-15; T 4, p 16
EP 852137	T 2, pp 41-46
EP 858318	T 1, p 6
EP 863145	Ex 1-11, pp 12-18
EP 895776	Comp. in rows 48-58, p 3; R 25+33, p 5
EP 911020	T 2, p 11-12
EP 916335	T 2-4, pp 19-41
EP 924246	T 2, p 9
EP 933376	Ex 1-15, pp 10-21
EP 944624	Ex 1+2, pp13-15
EP 945125	T 3 a+b, pp 14-15
EP 967200	Ex 2; T 3-5, pp 17-20
EP 969004	Ex 5, T 1, pp 6-8
JP 2000319629	CAS Regno. 80142-49-0, 137215-83-9, 307947-82-6
US 5635343	all compounds on pp 5-10
US 5338539	Ex 1-9, pp 3+4

**Table 2. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

The generic scope of the UV absorbers is described in the left-hand column; specific compounds are indicated in the right-hand column

US 5346691	Ex 40, p 7; T 5, p 8
US 5801244	Ex 1-5, pp 6-7
WO 0149686	Ex 1-5, pp 16-21
WO 0168047	Tables on pp 85-96
WO 0181297	Ex 1-3 pp 9-11
WO 0238537	All compounds p 3, compounds on rows 1-10 p 4
WO 9217461	Ex 1-22, pp 10-20
WO 9220690	Polymeric comp in examples 3-6
WO 9301164	T 1+2, pp 13-22
WO 9714680	Ex 1-3, p 10

The generic scope of the UV absorbers is described in the left column; specific compounds are indicated in the right column.

**Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
8	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
9	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
10	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts	56039-58-8
11	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione	70356-09-1

**Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

12	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate;	52793-97-2
22	3,3,5-Triethyl cyclohexyl-2-hydroxy benzoate	118-56-9
23	Isopentyl p-methoxycinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
28	Menthyl salicylate	89-46-3
29	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate	6197-30-4
30	2-ethylhexyl 4-(dimethylamino)benzoate	21245-02-3
31	2-ethylhexyl 4-methoxycinnamate	5466-77-3
32	2-ethylhexyl salicylate	118-60-5
33	Benzoic acid, 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)tris-, tris(2-ethylhexyl)ester; 2,4,6-Triphenyl-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine	88122-99-0
34	4-aminobenzoic acid	150-13-0
35	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
38	2-phenyl-1H-benzimidazole-5-sulphonic acid	27503-81-7
39	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
40	Triethanolamine salicylate	2174-16-5
41	3,3'-(1,4-phenylenedimethylene)bis[7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonic acid]	90457-82-2
42	Titanium dioxide	13463-67-7
44	Zinc oxide	1314-13-2
45	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol]	103597-45-1
46	2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-(1,3,5)-triazine	187393-00-6
47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
48	Benzoic acid, 4,4'-[[6-[[4-[[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester	154702-15-5
49	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-	155633-54-8
50	Dimethicodiethylbezalmalonate	207574-74-1
51	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt	92484-48-5

**Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

52	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester	302776-68-7
53	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]-propyl]N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1)	156679-41-3
54	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)amino]-, chloride	177190-98-6
55	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
56	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
57	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
58	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
59	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
60	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
61	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7
62	Benzenecetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
63	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
64	Anthralinic acid, p-menth-3-yl ester	134-09-8
65	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neoheliopan AP	349580-12-7,
66	1,3,5-Triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N''-(2-ethylhexyl)- or Uvasorb K2A	288254-16-0
67	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt ; Bisimidazylate; Neo Heliopan APC	180898-37-7

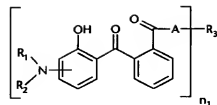
Suitable UV filter substances which can additionally be used with the UV absorbers according to the present invention are any UV-A and UV-B filter substances.

Preferably, the following UV filter combinations are of special interest:

- UV-filter combinations (A) comprising

(a.) at least one symmetrical triazine derivative of formula (1) and

(a<sub>2</sub>) at least one aminobenzophenone derivative of formula



wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are; C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>3</sub>-C<sub>10</sub>cycloalkyl; C<sub>3</sub>-C<sub>10</sub>cycloalkenyl; or R<sub>1</sub> and R<sub>2</sub> together with the linking nitrogen atom form a 5- or 6-membered heterocyclic ring;

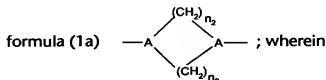
n<sub>1</sub> is a number from 1 to 4;

when n<sub>1</sub> = 1,

R<sub>3</sub> is a saturated or unsaturated heterocyclic radical; hydroxy-C<sub>1</sub>-C<sub>3</sub>alkyl; cyclohexyl optionally substituted with one or more C<sub>1</sub>-C<sub>3</sub>alkyl; phenyl optionally substituted with a heterocyclic radical, aminocarbonyl or C<sub>1</sub>-C<sub>3</sub>alkylcarboxy;

when n<sub>1</sub> is 2,

R<sub>3</sub> is an alkylene-, cycloalkylene, alkenylene or phenylene radical which is optionally substituted by a carbonyl- or carboxy group; a radical of formula  $\text{---CH}_2\text{---C}\equiv\text{C---CH}_2\text{---}$  or R<sub>3</sub> together with A forms a bivalent radical of the



n<sub>2</sub> is a number from 1 to 3;

when n<sub>1</sub> is 3,

R<sub>3</sub> is an alkanetriyl radical;

when n<sub>1</sub> is 4,

R<sub>3</sub> is an alkanetetrayl radical;

A is -O-; or -N(R<sub>3</sub>)-; and

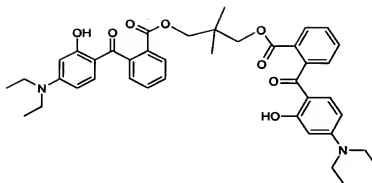
R<sub>3</sub> is hydrogen; C<sub>1</sub>-C<sub>3</sub>alkyl; or hydroxy-C<sub>1</sub>-C<sub>3</sub>alkyl.

Most preferred are UV-filter combinations (A1) comprising

(a<sub>2</sub>) the compound of formula (6); and



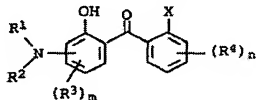
(a.) the compound of formula



- UV-filter combinations (B) comprising

(b<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and

(b<sub>2</sub>) at least one aminobenzophenone derivative of the formula



wherein

R<sup>1</sup>, R<sup>2</sup> independently from each other is hydrogen, C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>3</sub>-C<sub>10</sub>cycloalkenyl; wherein R<sup>1</sup> and R<sup>2</sup> may form a five- or six-membered ring;

R<sup>3</sup>, R<sup>4</sup> independently from each other is C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>3</sub>-C<sub>10</sub>cycloalkenyl, C<sub>1</sub>-C<sub>20</sub>alkoxy, C<sub>1</sub>-C<sub>20</sub>alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub>alkylamino, di(C<sub>1</sub>-C<sub>20</sub>alkyl)amino, optionally substituted aryl or Heteroaryl;

X is hydrogen; COOR<sup>5</sup>; CONR<sup>6</sup>R<sup>7</sup>

R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> independently from each other is hydrogen, C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>3</sub>-C<sub>10</sub>cycloalkyl; C<sub>3</sub>-C<sub>10</sub>cycloalkenyl; (Y-O)<sub>q</sub>-Z; optionally substituted Aryl

Y is -(CH<sub>2</sub>)<sub>2</sub>-; -(CH<sub>2</sub>)<sub>3</sub>-; -(CH<sub>2</sub>)<sub>4</sub>-; -CH(CH<sub>3</sub>)-CH<sub>2</sub>-;

Z is -CH<sub>2</sub>-CH<sub>2</sub>-; -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; CH(CH<sub>3</sub>)-CH<sub>2</sub>-;

m is 0; 1; 2; or \*;

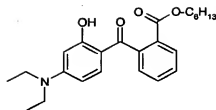
n is 0; 1; 2; 3; or 4; and

Q is a number from 1 to 20.

Most preferred are UV-filter combinations (B1) comprising

(b<sub>2</sub>) the compound of formula (6) and

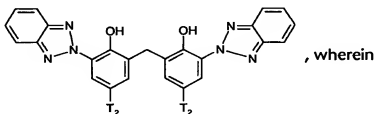
(b.) the compound of formula



- UV-filter combinations (C) comprising

(c.) at least one symmetrical triazine derivative of formula (1); and

(c.) at least one benzotriazole derivative of formula

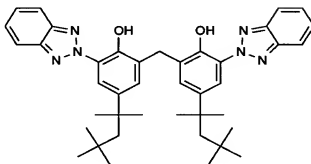


T<sub>2</sub> is C<sub>1</sub>-C<sub>10</sub>alkyl or phenyl-substituted C<sub>1</sub>-C<sub>4</sub>alkyl.

Most preferred are UV-filter combinations (C1) comprising

(c.) the compound of formula (6) and

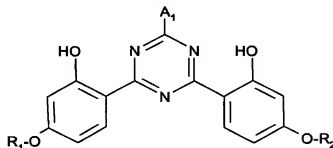
(c.) the compound of formula



- UV-filter combinations (D) comprising

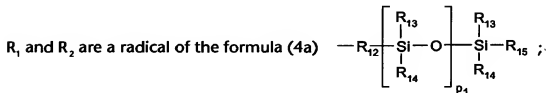
(d.) at least one symmetrical triazine derivative of formula (1); and

(d.) at least one compound of formula



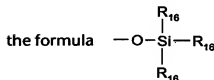
in which

$R_1$  and  $R_2$ , independently of one another, are  $C_3$ - $C_{10}$ alkyl;  $C_2$ - $C_{10}$ alkenyl; a radical of the formula  $-\text{CH}_2\text{-CH(OH)-CH}_2\text{-O-T}_1$  ; or



$R_{12}$  is a direct bond; a straight-chain or branched  $C_1$ - $C_6$ alkylene radical or a radical of the formula  $-\text{C}_{m_1}\text{H}_{2m_1}$  or  $-\text{C}_{m_1}\text{H}_{2m_1}\text{-O-}$  ;

$R_{13}$ ,  $R_{14}$  and  $R_{15}$ , independently of one another, are  $C_1$ - $C_{10}$ alkyl;  $C_1$ - $C_{10}$ alkoxy or a radical of

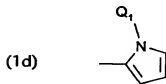
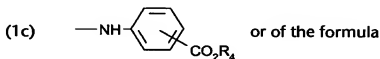
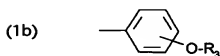


$R_{16}$  is  $C_1$ - $C_3$ alkyl;

$m_1$  and  $m_2$ , independently of one another, are 1 to 4;

$p_1$  is 0 or a number from 1 to 5;

$A_1$  is a radical of the formula



$R_3$  is hydrogen;  $C_1$ - $C_{10}$ alkyl,  $-(\text{CH}_2\text{CHR}_5\text{-O})_{n_1}\text{-R}_4$  ; or a radical of the formula

$-\text{CH}_2\text{-CH(OH)-CH}_2\text{-O-T}_1$ ;

$R_4$  is hydrogen;  $M$ ;  $C_1$ - $C_3$ alkyl; or a radical of the formula  $-(\text{CH}_2)_{m_2}\text{-O-T}_1$  ;

$R_5$  is hydrogen; or methyl;

$T_1$  is hydrogen; or  $C_1$ - $C_6$ alkyl;

Q, C<sub>1</sub>-C<sub>18</sub>alkyl;

M is a metal cation;

$m_j$  is 1 to 4; and

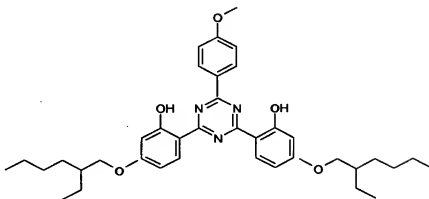
$n_i$  is 1-16.

Most preferred are UV-filter combinations (D1) comprising

(d<sub>3</sub>) the compound of formula (6) and

(d.) the compound of

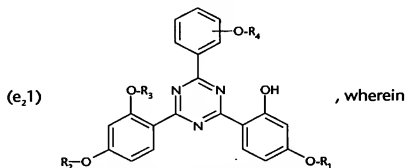
formula



- UV-filter combinations (E) comprising

(e.) at least one symmetrical triazine derivative of formula (1) and

(e.) at least one hydroxyphenyltriazine compound of formula



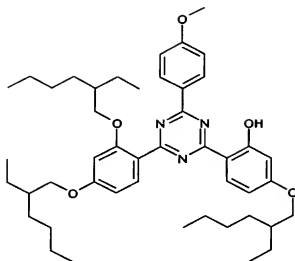
R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>18</sub>alkyl; C<sub>2</sub>-C<sub>10</sub>alkenyl; or phenyl-C<sub>1</sub>-C<sub>8</sub>alkyl;

R<sub>4</sub> is hydrogen; or C<sub>1</sub>-C<sub>5</sub>alkyl.

Most preferred are UV-filter combinations (D1) comprising

(d<sub>2</sub>) the compound of formula (6) and

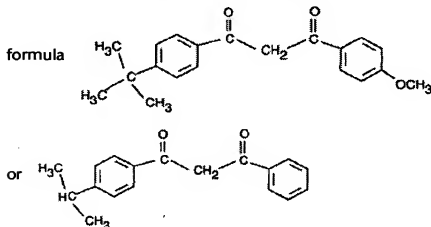
(d<sub>4</sub>) the compound of formula



- UV-filter combinations (F) comprising

(f<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and

(f<sub>2</sub>) at least one dibenzoylmethane derivative of



- UV-filter combinations (G) comprising

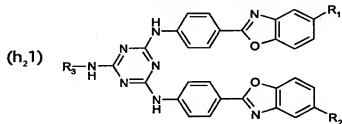
(g<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and

(g<sub>2</sub>) disodium phenyl dibenzimidazole tetrasulfonate (Heliopan AP).

- UV-filter combinations (H) comprising

(h<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and

(h<sub>2</sub>) at least one benzoxazole-substituted triazine of the formula



wherein

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently from each other are branched or unbranched C<sub>1</sub>-C<sub>12</sub>alkyl.

Preferred are UV-filter combinations (H1) comprising

(h<sub>1</sub>) the compound of formula (6) and

(h<sub>2</sub>) at least one of the compound of formula (h<sub>2</sub>1), wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are tert. butyl; or tert. amyl; and

R<sub>3</sub> is tert.butyl, tert.octyl; or 2-ethylhexyl.

Most preferred are UV-filter combinations (H2) comprising

(h<sub>1</sub>) the compound of formula (6) and

(h<sub>2</sub>) at least one of the compound of formula (h<sub>2</sub>1), wherein

(h<sub>2a</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.amyl; and R<sub>3</sub> is tert.butyl; or wherein

(h<sub>2b</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.butyl; and R<sub>3</sub> is tert.octyl; or

(h<sub>2c</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.butyl; and R<sub>3</sub> is 2-ethylhexyl; or wherein

(h<sub>2d</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.amyl; and R<sub>3</sub> is 2-ethylhexyl.

- UV-filter combinations (I) comprising

(i<sub>1</sub>) at least one symmetrical triazine derivative of formula (1) and

(i<sub>2</sub>) 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-.

- UV-filter combinations (K) comprising

(k<sub>1</sub>) at least one symmetrical triazine derivative of formula (1) and

(k<sub>2</sub>) siloxanes and silicones, di-Me, 1-[[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]phenoxy]methyl]ethenyl Me, 3-[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]phenoxy]-1-propenyl Me, Me hydrogen (dimethicodiethylbenzalmalonate; CAS-No. 207574-74-1)

The cosmetic or pharmaceutical preparations may be, for example, creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments. In addition to the above mentioned UV filters, the cosmetic or pharmaceutical preparations may contain further adjuvants as described below.

As water- and oil-containing emulsions (e.g. W/O, O/W, O/W/O and W/O/W emulsions or microemulsions) the preparations contain, for example, from 0.1 to 30 % by weight, preferably from 0.1 to 15 % by weight and especially from 0.5 to 10 % by weight, based on the total weight of the composition, of one or more UV absorbers, from 1 to 60 % by weight, especially from 5 to 50 % by weight and preferably from 10 to 35 % by weight, based on the total weight of the composition, of at least one oil component, from 0 to 30 % by weight, especially from 1 to 30 % by weight and preferably from 4 to 20 % by weight, based on the total weight of the composition, of at least one emulsifier, from 10 to 90 % by weight, especially from 30 to 90 % by weight, based on the total weight of the composition, of water, and from 0 to 88.9 % by weight, especially from 1 to 50 % by weight, of further cosmetically acceptable adjuvants.

The cosmetic or pharmaceutical compositions/preparations according to the invention may also contain one or one more additional compounds as described below.

#### Fatty alcohols

Guerbet alcohols based on fatty alcohols having from 6 to 18, preferably from 8 to 10 carbon atoms including cetyl alcohol, stearyl alcohol, cetearyl alcohol, oleyl alcohol, octyldodecanol, benzoate of C12-C15 alcohols, acetylated lanolin alcohol, etc..

#### Esters of fatty acids

Esters of linear  $C_6-C_{24}$  fatty acids with linear  $C_6-C_{24}$  alcohols, esters of branched  $C_6-C_{13}$  carboxylic acids with linear  $C_6-C_{24}$  fatty alcohols, esters of linear  $C_6-C_{24}$  fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched  $C_6-C_{22}$  fatty alcohols, especially dioctyl malates, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, for example caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid,

lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and technical-grade mixtures thereof (obtained, for example, in the pressure removal of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerisation of unsaturated fatty acids) with alcohols, for example, isopropyl alcohol, caproic alcohol, capryl alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linoyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical-grade mixtures thereof (obtained, for example, in the high-pressure hydrogenation of technical-grade methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fractions in the dimerisation of unsaturated fatty alcohols).

Examples of such ester oils are isopropylmyristate, isopropylpalmitate, isopropylstearate, isopropyl isostearate, isopropyloleate, n-butylstearate, n-hexyllaurate, n-decylolate, isooctylstearate, iso-nonylstearate, isononyl isononanoate, 2-ethylhexylpalmitate, 2-hexyllaurate, 2-hexyldecylstearate, 2-octyldodecylpalmitate, oleylolate, oleylerucate, erucylolate, erucyl-erucate, cetearyl octanoate, cetyl palmitate, cetyl stearate, cetyl oleate, cetyl behenate, cetyl acetate, myristyl myristate, myristyl behenate, myristyl oleate, myristyl stearate, myristyl palmitate, myristyl lactate, propylene glycol dicaprylate/caprate, stearyl heptanoate, diisostearyl malate, octyl hydroxystearate, etc..

#### Other adjuvants

alpha glucosylrutin (CAS No. 130603-71-3), 2-butyloctyl o-hydroxybenzoate (CAS No. 190085-41-7), vitamin E (CAS No. 1406-18-4), , vitamin E acetate (CAS No. 58-95-7), diethylhexyl 2,6- naphthalate, di-n-butyl adipate, di(2-ethylhexyl)-adipate, di(2-ethylhexyl)-succinate and diisotridecyl acelaat, and also diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di(2-ethylhexanoate), propylene glycol diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate. Esters of  $C_6-C_{24}$  fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, saturated and/or unsaturated, especially benzoic acid, esters of  $C_2-C_{12}$ dicarboxylic acids with linear or branched alcohols having from 1 to 22 carbon atoms or polyols having from 2



to 10 carbon atoms and from 2 to 6 hydroxy groups, or iminodisuccinic acid and iminodisuccinic acid salts [CAS 7408-20-0] or latex particles.

Natural or synthetic triglycerides including glyceryl esters and derivatives

Di- or tri-glycerides, based on  $C_6$ - $C_{18}$  fatty acids, modified by reaction with other alcohols (caprylic/capric triglyceride, wheat germ glycerides, etc.). Fatty acid esters of polyglycerin (polyglyceryl-n such as polyglyceryl-4 caprate, polyglyceryl-2 isostearate, etc. or castor oil, hydrogenated vegetable oil, sweet almond oil, wheat germ oil, sesame oil, hydrogenated cottonseed oil, coconut oil, avocado oil, corn oil, hydrogenated castor oil, shea butter, cocoa butter, soybean oil, mink oil, sunflower oil, safflower oil, macadamia nut oil, olive oil, hydrogenated tallow, apricot kernel oil, hazelnut oil, borago oil, etc.

Waxes including esters of long-chain acids and alcohols as well as compounds having wax-like properties, e.g., carnauba wax, beeswax (white or yellow), lanolin wax, candellila wax, ozokerite, japan wax, paraffin wax, microcrystalline wax, ceresin, cetearyl esters wax, synthetic beeswax, etc. Also, hydrophilic waxes as Cetearyl Alcohol or partial glycerides.

Pearlescent waxes:

alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polyvalent, unsubstituted or hydroxy-substituted carboxylic acids with fatty alcohols having from 6 to 22 carbon atoms, especially long-chained esters of tartaric acid; fatty substances, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, which in total have at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring-opening products of olefin epoxides having from 12 to 22 carbon atoms with fatty alcohols having from 12 to 22 carbon atoms and/or polyols having from 2 to 15 carbon atoms and from 2 to 10 hydroxy groups, and mixtures thereof.

Hydrocarbon oils:

Mineral oil (light or heavy), petrolatum (yellow or white), microcrystalline wax, paraffinic and isoparaffinic compounds, hydrogenated isoparaffinic molecules as polydecenes and polybu-

tene, hydrogenated polyisobutene, squalane, isohexadecane, isododecane and others from plant and animal kingdom.

#### Silicones or siloxanes (organosubstituted polysiloxanes)

Dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, and also amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds, which at room temperature may be in either liquid or resinous form. Linear polysiloxanes, dimethicone (Dow Corning 200 fluid, Rhodia Mirasil DM), dimethiconol, cyclic silicone fluids, cyclopentasiloxanes volatiles (Dow Corning 345 fluid), phenyltrimethicone (Dow Corning 556 fluid). Also suitable are simethicones, which are mixtures of dimethicones having an average chain length of from 200 to 300 dimethylsiloxane units with hydrogenated silicates. A detailed survey by Todd *et al.* of suitable volatile silicones may in addition be found in Cosm. Toil. 91, 27 (1976).

#### Fluorinated or perfluorinated oils

Perfluorohexane, dimethylcyclohexane, ethylcyclopentane, polyperfluoromethylisopropyl ether.

#### Emulsifiers

Any conventionally usable emulsifier can be used for the compositions. Emulsifier systems may comprise for example: carboxylic acids and their salts: alcalin soap of sodium, potassium and ammonium, metallic soap of calcium or magnesium, organic basis soap such as Lauric, palmitic, stearic and oleic acid etc... Alkyl phosphates or phosphoric acid esters, acid phosphate, diethanolamine phosphate, potassium cetyl phosphate. Ethoxylated carboxylic acids or polyethyleneglycol esters, PEG-n acylates. Linear fatty alcohols having from 8 to 22 carbon atoms, branched from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol propylene oxide with with fatty acids having from 12 to 22 carbon atoms and with alkylphenols having from 8 to 15 carbon atoms in the alkyl group. Fatty alcohol polyglycoether such as laureth-n, ceteareth-n, steareth-n, oleth-n. Fatty acid polyglycoether such as PEG-n stearate, PEG-n oleate, PEG-n cocoate. Monoglycerides and polyol esters. C12-C22 fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide with polyols. Fatty acid and polyglycerol ester such as monostearate glycerol, diisostearoyl polyglyceryl-3-diisostearates, polyglyceryl-3-diisostearates, triglyceryl diisostearates, polyglyceryl-2-sesquiisostearates or

polyglyceryl dimerates. Mixtures of compounds from a plurality of those substance classes are also suitable. Fatty acid polyglycolesters such as monostearate diethylene glycol, fatty acid and polyethylene glycol esters, fatty acid and saccharose esters such as sucro esters, glycerol and saccharose esters such as sucro glycerides. Sorbitol and sorbitan, sorbitan mono- and di-esters of saturated and unsaturated fatty acids having from 6 to 22 carbon atoms and ethylene oxide addition products. Polysorbate-n series, sorbitan esters such as sesquisteate, sorbitan, PEG-(6)-isosteate sorbitan, PEG-(10)-sorbitan laurate, PEG-17-dioleate sorbitan. Glucose derivatives, C8-C22 alkyl-mono and oligo-glycosides and ethoxylated analogues with glucose being preferred as the sugar component. O/W emulsifiers such as methyl gluceth-20 sesquisteate, sorbitan stearate/sucrose cocoate, methyl glucose sesquisteate, cetearyl alcohol/cetearyl glucoside. W/O emulsifiers such as methyl glucose dioleate/ methyl glucose isosteate. Sulfates and sulfonated derivatives, dialkylsulfosuccinates, dioctyl succinate, alkyl lauryl sulfonate, linear sulfonated paraffins, sulfonated tetrapropylene sulfonate, sodium lauryl sulfates, ammonium and ethanolamine lauryl sulfates, lauryl ether sulfates, sodium laureth sulfates, sulfosuccinates, acetyl isothionates, alkanolamide sulfates, taurines, methyl taurines, imidazole sulfates. Amine derivatives, amine salts, ethoxylated amines, oxide amine with chains containing an heterocycle such as alkyl imidazolines, pyridine derivatives, isoquinoline, cetyl pyridinium chloride, cetyl pyridinium bromide, quaternary ammonium such as cetyltrimethylbromide ammonium bromide (CTBA), stearyl-alkonium. Amide derivatives, alkanolamides such as acylamide DEA, ethoxylated amides such as PEG-n acylamide, oxydeamide. Polysiloxane/polyalkyl/polyether copolymers and derivatives, dimethicone, copolyols, silicone polyethylene oxide copolymer, silicone glycol copolymer. Propoxylated or POE-n ethers (Meroxapols), Polaxamers or poly(oxyethylene)-m-block-poly(oxypropylene)-n-block(oxyethylene). Zwitterionic surfactants that carry at least one quaternary ammonium group and at least one carboxylate and/or sulfonate group in the molecule. Zwitterionic surfactants that are especially suitable are betaines, such as N-alkyl-N,N-dimethylammonium glycinate, cocoalkyldimethylammonium glycinate, N-acylamino-propyl-N,N-dimethylammonium glycinate, cocoacylamino-propyldimethylammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethylglycinate, N-alkylbetaine, N-alkylaminobetaines. Alkylimidazolines, alkylpeptides, liposaminic acids, self emulsifying bases and the compounds as described in K.F.DePolo, A short textbook of cosmetology, Chapter 8, Table 8-7, p250-251.

Non ionic emulsifiers such as PEG-6 beeswax (and) PEG-6 stearate (and) polyglyceryl -2-iso-stearate [Apifac], glyceryl stearate ( and) PEG-100 stearate. [Arlacel 165], PEG-5 glyceryl stearate [arlatone 983 S], sorbitan oleate (and) polyglyceryl-3 ricinoleate.[Arlacel 1689], sorbitan stearate and sucrose cocoate [arlatone 2121], glyceryl stearate and laureth-23 [Cerasynth 945], cetearyl alcohol and ceteth-20 [Cetomacrogol Wax], cetearyl alcohol and coly sorbate 60 and PEG-150 and stearate-20[Polawax GP 200, Polawax NF], cetearyl alcohol and cetearyl polyglucoside [Emulgade PL 1618], cetearyl alcohol and ceteareth-20 [Emulgade 1000NI, Cosmowax], cetearyl alcohol and PEG-40 castor oil [Emulgade F Special], cetearyl alcohol and PEG-40 castor oil and sodium cetearyl sulfate [Emulgade F], stearyl alcohol and steareth-7 and steareth-10 [Emulgator E 2155], cetearyl alcohol and steareth-7 and steareth-10 [Emulsifying wax U.S.N.F], glyceryl stearate and PEG-75 stearate [Gelot 64], propylene glycol ceteth-3 acetate .[Hetester PCS], propylene glycol isoceth-3 acetate [Hetester PHA], cetearyl alcohol and ceteth-12 and oleth-12 [Lanbriol Wax N 21], PEG -6 stearate and PEG-32 stearate [Tefose 1500], PEG-6 stearate and ceteth-20 and steareth-20 [Tefose 2000], PEG-6 stearate and ceteth-20 and glyceryl stearate and steareth-20 [Tefose 2561], glyceryl stearate and ceteareth-20 [Teginacid H, C, X].

Anionic emulsifiers such as PEG-2 stearate SE, glyceryl stearate SE [Monelgine, Cutina KD], propylene glycol stearate [Tegin P], cetearyl Alcohol and Sodium cetearyl sulfate [Lanette N, Cutina LE, Crodacol GP], cetearyl alcohol and sodium lauryl sulfate [Lanette W], trianeth-4 phosphatate and glycol stearate and PEG-2 stearate [Sedefos 75], glyceryl stearate and sodium lauryl Sulfate [Teginacid Special]. Cationic acid bases such as cetearyl alcohol and cetrimonium bromide.

The emulsifiers may be used in an amount of, for example, from 1 to 30 % by weight, especially from 4 to 20 % by weight and preferably from 5 to 10 % by weight, based on the total weight of the composition.

When formulated in O/W emulsions, the preferably amount of such emulsifier system could represent 5% to 20% of the oil phase.

### Adjuvants and additives

The cosmetic / pharmaceutical preparations, for example creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments, may in addition contain, as further adjuvants and additives, mild surfactants, super-fatting agents, consistency regulators, thickeners, polymers, stabilisers, biogenic active ingredients, deodorising active ingredients, anti-dandruff agents, film formers, swelling agents, further UV light-protective factors, antioxidants, hydrotropic agents, preservatives, insect repellents, self-tanning agents, solubilisers, perfume oils, colourants, bacteria-inhibiting agents and the like.

### Super-fatting agents

Substances suitable for use as super-fatting agents are, for example, lanolin and lecithin and also polyethoxylated or acrylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the latter simultaneously acting as foam stabilisers.

### Surfactants

Examples of suitable mild surfactants, that is to say surfactants especially well tolerated by the skin, include fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or di-alkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid tau-rides, fatty acid glutamates,  $\alpha$ -olefin sulfonates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensation products, the latter preferably being based on wheat proteins.

### Consistency regulators/thickeners and rheology modifiers

Silicium dioxide, magnesium silicates, aluminium silicates, polysaccharides or derivatives thereof for example hyaluronic acid, xanthan gum, guar-guar, agar-agar, alginates, carrageenan, gellan, pectines, or modified cellulose such as hydroxycellulose, hydroxypropyl-methylcellulose. In addition polyacrylates or homopolymer of reticulated acrylic acids and polyacrylamides, carbomer (carbopol types 980, 981, 1382, ETD 2001, ETD2020, Ultrez 10) or Salcare range such as Salcare SC80(stearth-10 allyl ether/acrylates copolymer), Salcare SC81(acrylates copolymer), Salcare SC91 and Salcare AST(sodium acrylates copolymer/PPG-1 trideceth-6), sepiigel 305(polyacrylamide/laureth-7), Simulgel NS and Simulgel EG (hydro-

xyethyl acrylate / sodium acryloyldimethyl taurate copolymer), Stabilen 30 (acrylates / vinyl isodecanoate crosspolymer), Pemulen TR-1 (acrylates / C10-30 alkyl acrylate crosspolymer), Luvigel EM (sodium acrylates copolymer), Aculyn 28 (acrylates/beheneth-25 methacrylate copolymer), etc.

### Polymers

Suitable cationic polymers are, for example, cationic cellulose derivatives, for example a quaternised hydroxymethyl cellulose obtainable under the name Polymer JR 400 from Amerchol, cationic starches, copolymers of diallylammonium salts and acrylamides, quarternised vinylpyrrolidone/vinyl imidazole polymers, for example Luviquat® (BASF), condensation products of polyglycols and amines, quaternised collagen polypeptides, for example lauryldimonium hydroxypropyl hydrolyzed collagen (Lamequat®L/Grünau), quaternised wheat polypeptides, polyethyleneimine, cationic silicone polymers, for example amidomethicones, copolymers of adipic acid and dimethylaminoxypropyldiethylenetriamine (Cartaretin/Sandoz), copolymers of acrylic acid with dimethyldiallylammonium chloride (Merquat 550 / Chemviron), polyaminopolyamides, as described, for example, in FR-A-2 252 840, and the crosslinked water-soluble polymers thereof, cationic chitin derivatives, for example of quaternised chitosan, optionally distributed as microcrystals; condensation products of dihaloalkyls, for example dibromobutane, with bisdialkylamines, for example bisdimethylamino-1,3-propane, cationic guar gum, for example Jaguar C-17, Jaguar C-16 from Celanese, quaternised ammonium salt polymers, for example Mirapol A-15, Mirapol AD-1, Mirapol AZ-1 from Miranol. As anionic, zwitterionic, amphoteric and non-ionic polymers there come into consideration, for example, vinyl acetate / crotonic acid copolymers, vinylpyrrolidone / vinyl acrylate copolymers, vinyl acetate / butyl maleate / isobornyl acrylate copolymers, methyl vinyl ether / maleic anhydride copolymers and esters thereof, uncrosslinked polyacrylic acids and polyacrylic acids crosslinked with polyols, acrylamidopropyl-trimethylammonium chloride /acrylate copolymers, octyl acrylamide/methyl methacrylate-tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and also optionally derivatised cellulose ethers and silicones. Furthermore the polymers as described in EP 1093796 (pages 3-8, paragraphs 17-68) may be used.

### Biogenic active ingredients

Biogenic active ingredients are to be understood as meaning, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes.

### Deodorising active ingredients

As deodorising active ingredients there come into consideration, for example, anti-perspirants, for example aluminium chlorohydrates (see J. Soc. Cosm. Chem. 24, 281 (1973)). Under the trade mark Locron® of Hoechst AG, Frankfurt (FRG), there is available commercially, for example, an aluminium chlorohydrate corresponding to formula  $Al_2(OH)_2Cl \times 2.5 H_2O$ , the use of which is especially preferred (see J. Pharm. Pharmacol. 26, 531 (1975)). Besides the chlorohydrates, it is also possible to use aluminium hydroxyacetates and acidic aluminium/zirconium salts. Esterase inhibitors may be added as further deodorising active ingredients. Such inhibitors are preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and especially triethyl citrate (Hydagen CAT, Henkel), which inhibit enzyme activity and hence reduce odour formation. Further substances that come into consideration as esterase inhibitors are sterol sulfates or phosphates, for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfate or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester and hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial active ingredients that influence the germ flora and kill or inhibit the growth of sweat-decomposing bacteria can likewise be present in the preparations (especially in stick preparations). Examples include chitosan, phenoxyethanol and chlorhexidine gluconate. 5-chloro-2-(2,4-dichlorophenoxy)-phenol (Triclosan, Irgasan, Ciba Specialty Chemicals Inc.) has also proved especially effective.

### Anti-dandruff agents

As anti-dandruff agents there may be used, for example, climbazole, octopirox and zinc pyri-thione. Customary film formers include, for example, chitosan, microcrystalline chitosan, quaternised chitosan, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers,

polymers of quaternary cellulose derivatives containing a high proportion of acrylic acid, collagen, hyaluronic acid and salts thereof and similar compounds.

### Antioxidants

In addition to the primary light-protective substances it is also possible to use secondary light-protective substances of the antioxidant kind that interrupt the photochemical reaction chain triggered when UV radiation penetrates the skin or hair. Typical examples of such antioxidants are amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotinoids, carotenes, lycopene and derivatives thereof, chlorogenic acid and derivatives thereof, liponic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglyucose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl, lauryl, palmitoyl, oleyl, linoleyl, cholesteryl and glyceryl esters thereof) and also salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and also sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, hepta-thionine sulfoximine), also (metal) chelating agents (e.g. hydroxy fatty acids, palmitic acid phytic acid, lactoferrin), hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EDDS, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, magnesium ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (e.g. vitamin A palmitate) and also coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, glycosylrutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, superoxide dismutase, N-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]sulfanilic acid (and salts thereof, for example the disodium salts), zinc and derivatives thereof (e.g. ZnO, ZnSO<sub>4</sub>), selenium and derivatives thereof (e.g. selenium methionine), stilbene and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide) and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides,



nucleosides, peptides and lipids) of those mentioned active ingredients. HALS ("Hindered Amine Light Stabilizers") compounds may also be mentioned.

Further synthetic and natural antioxidants are listed e.g. in patent WO 0025731:

Structures 1-3 (page 2), structure 4 (page 6), structures 5-6 (page 7) and compounds 7-33 (page 8-14).

The amount of antioxidants present is usually from 0.001 to 30 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV absorber of formula (1).

#### Hydrotropic agents

To improve the flow behaviour it is also possible to employ hydrotropic agents, for example ethoxylated or non ethoxylated mono-alcohols, diols or polyols with a low number of carbon atoms or their ethers (e.g. ethanol, isopropanol, 1,2-dipropanediol, propyleneglycol, glycerin, ethylene glycol, ethylene glycol monoethylether, ethylene glycol monobutylether, propylene glycol monomethylether, propylene glycol monoethylether, propylene glycol monobutylether, diethylene glycol monomethylether; diethylene glycol monoethylether, diethylene glycol monobutylether and similar products). The polyols that come into consideration for that purpose have preferably from 2 to 15 carbon atoms and at least two hydroxy groups. The polyols may also contain further functional groups, especially amino groups, and/or may be modified with nitrogen. Typical examples are as follows: glycerol, alkylene glycols, for example ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and also polyethylene glycols having an average molecular weight of from 100 to 1000 Dalton; technical oligoglycerol mixtures having an intrinsic degree of condensation of from 1.5 to 10, for example technical diglycerol mixtures having a diglycerol content of from 40 to 50 % by weight; methylol compounds, such as, especially, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol and dipentaerythritol; lower alkyl-glucosides, especially those having from 1 to 8 carbon atoms in the alkyl radical, for example methyl and butyl glucoside; sugar alcohols having from 5 to 12 carbon atoms, for example sorbitol or mannitol; sugars having from 5 to 12 carbon atoms, for example glucose or saccharose; amino sugars, for example glucamine; dialcohol amines, such as diethanolamine or 2-amino-1,3-propanediol.

#### Preservatives and Bacteria-inhibiting agents

Suitable preservatives include, for example, Methyl-, Ethyl-, Propyl-, Butyl- parabens, Benzalkonium chloride, 2-Bromo-2-nitro-propane-1,3-diol, Dehydroacetic acid, Diazolidinyl Urea, 2-Dichloro-benzyl alcohol, DMDM hydantoin, Formaldehyde solution, Methylidibromoglutanitrile, Phenoxyethanol, Sodium Hydroxymethylglycinate, Imidazolidinyl Urea, Triclosan and further substance classes listed in the following reference: K.F.DePolo – A short textbook of cosmetology, Chapter 7, Table 7-2, 7-3, 7-4 and 7-5, p210-219.

#### Bacteria-inhibiting agents

Typical examples of bacteria-inhibiting agents are preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monolaurate has also proved to be a bacteriostatic agent. The amount of the additional bacteria-inhibiting agents present is usually from 0.1 to 2 % by weight, based on the solids content of the preparations.

#### Perfume oils

There may be mentioned as perfume oils mixtures of natural and/or synthetic aromatic substances. Natural aromatic substances are, for example, extracts from blossom (lilies, lavender, roses, jasmine, neroli, ylang-ylang), from stems and leaves (geranium, patchouli, petitgrain), from fruit (aniseed, coriander, caraway, juniper), from fruit peel (bergamot, lemons, oranges), from roots (mace, angelica, celery, cardamom, costus, iris, calmus), from wood (pine-wood, sandalwood, guaiacum wood, cedarwood, rosewood), from herbs and grasses (tarragon, lemon grass, sage, thyme), from needles and twigs (spruce, pine, Scots pine, mountain pine), from resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials also come into consideration, for example civet and castoreum. Typical synthetic aromatic substances are, for example, products of the ester, ether, aldehyde, ketone, alcohol or hydrocarbon type. Aromatic substance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl

acetate, dimethylbenzylcarbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having from 8 to 18 hydrocarbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, linal and bourgeonal; the ketones include, for example, the ionones, isomethylionone and methyl cedryl ketone; the alcohols include, for example, anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenyl ethyl alcohol and terpinol; and the hydrocarbons include mainly the terpenes and balsams. It is preferable, however, to use mixtures of various aromatic substances that together produce an attractive scent. Ethereal oils of relatively low volatility, which are chiefly used as aroma components, are also suitable as perfume oils, e.g. sage oil, camomile oil, clove oil, melissa oil, oil of cinnamon leaves, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil. Preference is given to the use of bergamot oil, dihydromyrcenol, linal, lyral, citronellol, phenyl ethyl alcohol, hexyl cinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, boisambrene forte, ambroxan, indole, hedione, sandelice, lemon oil, tangerine oil, orange oil, allyl amyl glycolate, cyclovertal, lavandin oil, muscatel sage oil, damascone, bourbon geranium oil, cyclohexyl salicylate, vertofix coeur, iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat alone or in admixture with one another.

### Colourants

There may be used as colourants the substances that are suitable and permitted for cosmetic purposes, as compiled, for example, in the publication "Kosmetische Färbemittel" of the Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106. The colourants are usually used in concentrations of from 0.001 to 0.1 % by weight, based on the total mixture.

### Other adjuvants

It is furthermore possible for the cosmetic preparations to contain, as adjuvants, anti-foams, such as silicones, *structurants*, such as maleic acid, *solubilisers*, such as ethylene glycol, propylene glycol, glycerol or diethylene glycol, opacifiers, such as latex, styrene/PVP or styrene/acrylamide copolymers, complexing agents, such as EDTA, NTA, alaninediacetic acid or

phosphonic acids, *propellants*, such as propane/butane mixtures,  $N_2O$ , dimethyl ether,  $CO_2$ ,  $N_2$  or air, so-called coupler and developer components as oxidation dye precursors, *reducing agents*, such as thioglycolic acid and derivatives thereof, thiolactic acid, cysteamine, thio-malic acid or mercaptoethanesulfonic acid, or oxidising agents, such as hydrogen peroxide, potassium bromate or sodium bromate.

Suitable insect repellents are, for example, N,N-diethyl-m-toluamide, 1,2-pentanediol or insect repellent 3535; suitable self-tanning agents are, for example, dihydroxyacetone and/or erythrose or dihydroxy acetone and/or dihydroxy acetone precursors as described in WO 01/85124 and/or erythrose.

#### Polymeric beads or hollow spheres as SPF enhancers

The combination of the UV-absorbers and UV-absorber combinations, listed above, with SPF enhancers, such as non-active ingredients like Styrene/acrylates copolymer, silica beads, spheroidal magnesium silicate, crosslinked Polymethylmethacrylates (PMMA ; Micoppearl M305 Seppic), can maximize better the UV protection of the sun products. Holosphere additives (Sunsphere®ISP, Silica Shells Kobo.) deflect radiation and the effective path length of the photon is therefore increased.( EP0893119). Some beads, as mentioned previously, provide a soft feel during spreading. Moreover, the optical activity of such beads, e.g.Micoppearl M305, can modulate skin shine by eliminating reflection phenomena and indirectly may scatter the UV light.

#### Cosmetic or pharmaceutical preparations

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations. There come into consideration, for example, especially the following preparations:

- skin-care preparations, e.g. skin-washing and cleansing preparations in the form of tablet-form or liquid soaps, soapless detergents or washing pastes,
- bath preparations, e.g. liquid (foam baths, milks, shower preparations) or solid bath preparations, e.g. bath cubes and bath salts;
- skin-care preparations, e.g. skin emulsions, multi-emulsions or skin oils;

- cosmetic personal care preparations, e.g. facial make-up in the form of day creams or powder creams, face powder (loose or pressed), rouge or cream make-up, eye-care preparations, e.g. eyeshadow preparations, mascara, eyeliner, eye creams or eye-fix creams; lip-care preparations, e.g. lipsticks, lip gloss, lip contour pencils, nail-care preparations, such as nail varnish, nail varnish removers, nail hardeners or cuticle removers;
- foot-care preparations, e.g. foot baths, foot powders, foot creams or foot balsams, special deodorants and antiperspirants or callus-removing preparations;
- light-protective preparations, such as sun milks, lotions, creams or oils, sunblocks or tropicals, pre-tanning preparations or after-sun preparations;
- skin-tanning preparations, e.g. self-tanning creams;
- depigmenting preparations, e.g. preparations for bleaching the skin or skin-lightening preparations;
- insect-repellents, e.g. insect-repellent oils, lotions, sprays or sticks;
- deodorants, such as deodorant sprays, pump-action sprays, deodorant gels, sticks or roll-ons;
- antiperspirants, e.g. antiperspirant sticks, creams or roll-ons;
- preparations for cleansing and caring for blemished skin, e.g. synthetic detergents (solid or liquid), peeling or scrub preparations or peeling masks;
- hair-removal preparations in chemical form (depilation), e.g. hair-removing powders, liquid hair-removing preparations, cream- or paste-form hair-removing preparations, hair-removing preparations in gel form or aerosol foams;
- shaving preparations, e.g. shaving soap, foaming shaving creams, non-foaming shaving creams, foams and gels, preshave preparations for dry shaving, aftershaves or aftershave lotions;
- fragrance preparations, e.g. fragrances (eau de Cologne, eau de toilette, eau de parfum, parfum de toilette, perfume), perfume oils or perfume creams;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen

peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

#### Presentation forms

The final formulations listed may exist in a wide variety of presentation forms, for example:

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,
- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- in the form of a foam, or
- in the form of a paste.

Of special importance as cosmetic preparations for the skin are light-protective preparations, such as sun milks, lotions, creams, oils, sunblocks or tropicals, pretanning preparations or after-sun preparations, also skin-tanning preparations, for example self-tanning creams. Of particular interest are sun protection creams, sun protection lotions, sun protection milk and sun protection preparations in the form of a spray.

Of special importance as cosmetic preparations for the hair are the above-mentioned preparations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-straightening preparations, liquid hair-setting preparations, hair foams and hairsprays. Of special interest are hair-washing preparations in the form of shampoos.

A shampoo has, for example, the following composition: from 0.01 to 5 % by weight of a UV absorber according to the invention, 12.0 % by weight of sodium laureth-2-sulfate, 4.0

% by weight of cocamidopropyl betaine, 3.0 % by weight of sodium chloride, and water ad 100%.

For example, especially the following hair-cosmetic formulations may be used:

- a,) spontaneously emulsifying stock formulation, consisting of the UV absorber according to the invention, PEG-6-C<sub>10</sub>oxoalcohol and sorbitan sesquioleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- a,) spontaneously emulsifying stock formulation consisting of the UV absorber according to the invention, tributyl citrate and PEG-20-sorbitan monooleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- b) quat-doped solutions of the UV absorber according to the invention in butyl triglycol and tributyl citrate;
- c) mixtures or solutions of the UV absorber according to the invention with n-alkylpyrrolidone.

Other typical ingredients in such formulations are preservatives, bactericides and bacteriostatic agents, perfumes, dyes, pigments, thickening agents, moisturizing agents, humectants, fats, oils, waxes or other typical ingredients of cosmetic and personal care formulations such as alcohols, poly-alcohols, polymers, electrolytes, organic solvents, silicon derivatives, emollients, emulsifiers or emulsifying surfactants, surfactants, dispersing agents, antioxidants, anti-irritants and anti-inflammatory agents etc.

Examples of cosmetic and pharmaceutical preparations (X = preferred combinations)

O/W systems:

Ingredients	1	2	3	4	5	6	7	8
<b>Emulsifiers</b>								
Potassium Cetyl Phosphate 2%-5%	X							
Cetearyl Alcohol/ Dicapryl Phosphate/Ceteth-10 Phosphate 2%-6%		X						
Sodium Stearyl Phthalamate 1%-2%			X					
Cetearyl Alcohol/Behentrimonium Methosulfate 1%-5%				X				
Quaternium-32 1%-5%					X			

Ingredients	1	2	3	4	5	6	7	8
Dimethicone copolyol/ Caprylic/Capric Triglyceride 1%-4%						X		
Steareth-2 /Steareth-21 2%-5%							X	
Polyglyceryl Methyl Glucose Distearate 1%-4%								X
Lipophilic emollient/dispersant oil 15%-20%	X	X	X	X	X	X	X	X
Fatty Alcohols and/or Waxes 1%-5%	X	X	X	X	X	X	X	X
Thickeners (water swellable thickeners) 0.5% - 1.5%	X	X	X	X	X	X	X	X
Preservatives 0.5% - 1%	X	X	X	X	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1% - 0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 0,1% - 20%	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X	X	X

#### W/O systems

Ingredients	1	2	3	4	5
Emulsifiers	X	X	X	X	X
Polyglyceryl-2 Dipolyhydroxystearate 2%-4%	X	X	X	X	X
PEG-30 Dipolyhydroxystearate 2%-4%		X			
Rapeseed Oil Sorbitol Esters 1%-5%			X		
PEG-45/Dodecyl Glycol Copolymer 1%-5%				X	
Sorbitan Oleate / Polycerol-3 ricinoleate 1%-5%					X
Lipophilic emollient/dispersant oil 10% - 20%	X	X	X	X	X
Fatty Alcohols and/or Waxes 10% - 15%	X	X	X	X	X
Electrolytes (NaCl, MgSO <sub>4</sub> ) 0.5% - 1%	X	X	X	X	X
Polyol phase (Propylene glycol, glycerin) 1% - 8%	X	X	X	X	X
Preservatives 0.3% - 0.8%	X	X	X	X	X
Perfume oils 0.1% - 0.4%	X	X	X	X	X
Chelating agents (such as EDTA) 0% - 0.2%	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X
UV-absorber according to the invention 0,1% - 20%.	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%.	X	X	X	X	X

#### W/Silicone systems

Ingredients	1	2	3	4
Emulsifiers				
Dimethicone Copolyol / Cyclomethicone 5%-10%		X		X
Laurylmethicone Copolyol 5%-10%			X	X
Silicone phase				



Cyclopentasiloxane 15%-25%	X			X
Dimethicone 15%-25%		X	X	
<u>Silicone elastomer</u>				
Dimethicone/Vinyldimethicone Crosspolymer 1%-10%	X	X	X	X
Humectant/polyols (Propylene glycol, glycerin...) 2%-8%	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X
Preservatives 0.3%-0.8%	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X
Water deionized Qs 100%	X	X	X	X
UV-absorber according to the invention 0,1% - 20%	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X

### Multiple emulsions

[illegible]

Ingredients	1	2	3	4	5	6	7	8	9	10	11	12
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 0.1%-20%	X	X	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X	X	X	X	X	X	X

#### O1/W/O2 emulsions

Ingredients	1	2	3	4	5	6	7	8
Primary emulsion O1/W								
PEG-60 Hydrogenated Castor Oil 25%	X			X	X			X
Stearth-25 25%		X	X			X	X	
Oil phase 75%								
Fatty acid esters	X		X					
Natural and synthetic Triglycerides		X		X				
Hydrocarbon oils					X		X	
Silicone oils						X		X
Preservatives 0.3% - 0.8%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Non ionic multifunctional W/O emulsifier 2%-5%	X	X	X	X	X	X	X	X
Waxes 1%-5%	X	X	X	X	X	X	X	X
Oil phase 20%-30%	X	X	X	X	X	X	X	X
Fatty acid esters								
Natural and synthetic Triglycerides								
Hydrocarbon oils								
Silicone oils								
Primary emulsion O1/W 15%	X	X	X	X	X	X	X	X
Electrolytes (NaCl, MgSO <sub>4</sub> ) 0.1%-0.5%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 0.1%-20%	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X

#### Microemulsions

Ingredients	1	2	3	4	5	6	7	8	9	10
Surfactants										
PEG-8 Caprylic/Capric Glycerides 10%-25%	X			X	X			X	X	
PPG-5-ceteth-20 10%-25%		X	X			X	X			X
Co-surfactants										
Polyglyceryl-6 Isostearate 5%-15%	X		X							
Polyglyceryl-3 Diisostearate 5%-15%		X		X						

Ingredients	1	2	3	4	5	6	7	8	9	10
Polyglyceryl-6 Dioleate 5%-15%					X		X			
PPG-10 Cetyl Ether 5%-15%						X		X		
Ethoxydiglycol 5%-15%									X	X
Oil phase 10%-80%	X	X	X	X	X	X	X	X	X	X
Isostearyl Benzoate	X	X	X	X	X	X	X	X	X	X
Isostearyl Isostearate	X	X	X	X	X	X	X	X	X	X
PEG-7 Glyceryl Cocoate	X	X	X	X	X	X	X	X	X	X
Cyclomethicone	X	X	X	X	X	X	X	X	X	X
Polyalcohols/Humectants 1%-10%	X	X	X	X	X	X	X	X	X	X
Preservatives 0.3 -0.8%	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 0,1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X

#### O/W Spray emulsions

Ingredients	1	2	3	4	5	6
Emulsifiers						
Alkyl Phosphates 0.1%-5%	X			X	X	
Glucosidic derivatives 0.1%-5%			X	X		X
Solubilisants						
Ethoxylated Glyceryl ethers 0.1%-1%	X		X			
Polysorbates 0.1%-1%		X		X		
Ethoxylated Oleyl ethers 0.1%-1%					X	X
Film forming agents						
PVP/VA Copolymer 1%-10%	X		X		X	
PVM/MA Copolymer 1%-10%		X		X		X
Oil phase 5%-20%	X	X	X	X	X	X
Natural oils(Meadowfoam, Jojoba, Macadamia...)	X	X	X	X	X	X
Fatty acids esters	X	X	X	X	X	X
Mineral oils	X	X	X	X	X	X
Silicone oils	X	X	X	X	X	X
Alcohol 0%-50%	X	X	X	X	X	X
Thickeners 0.1%-0.5%	X	X	X	X	X	X
Polyacrylates	X	X	X	X	X	X
Aluminium/Magnesium Silicates	X	X	X	X	X	X
Gums	X	X	X	X	X	X
Neutralizing agents 0%-1%	X	X	X	X	X	X
Polyalcohols/Humectants 1%-5%	X	X	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X
Perfume oils 0.1%- 0.5%	X	X	X	X	X	X

Ingredients	1	2	3	4	5	6
Preservatives 0.4%-1%	X	X	X	X	X	X
UV-absorber according to the invention 0,1% - 20%	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X

**G – Aqueous**

Ingredients	1	2	3	4	5	6	7	8	9	10	11	12
Thickeners												
Natural Thickener 1%-5%	X					X	X					X
Semi-synthetic Thickener 1%-5%		X			X			X			X	
Synthetic Thickener 0.3% - 1.3%			X	X					X	X		
Neutralizing Agents 0.5% - 1.5%	X	X	X	X	X	X	X	X	X	X	X	X
Polyols – Humectants 5%-50%	X	X	X	X	X	X	X	X	X	X	X	X
Film forming agent/Conditioner												
Polyquaternium series 1%-5%	X	X	X				X	X	X			
PVM/MA Copolymer 1%-5%				X	X	X				X	X	X
Preservatives 0.5%-1%	X	X	X	X	X	X	X	X	X	X	X	X
Chelating Agents (as EDTA) < 0.1%	X	X	X	X	X	X	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.05%-0.4%	X	X	X	X	X	X	X	X	X	X	X	X
Solubilisants												
Ethoxylated Glyceryl ethers 0.1%-5%	X	X	X									
Polysorbates 0.1%-5%				X	X	X						
Ethoxylated Oleyl ethers 0.1%-5%							X	X	X	X	X	X
UV-absorber according to the invention 0,1%-20%	X	X	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X	X	X

**Oleogels**

Ingredients	1	2	3	4	5	6	7	8	9	10
Thickeners										
Hydrogenated Lecithin 1%-10%	X									X
Silica Dimethyl Silylate 1%-10%		X							X	
Silica 1%-5%			X					X		
C <sub>24-28</sub> Alkyl Dimethicone 1%-5%				X			X			
Aluminium or Magnesium Stearate 1%-5%						X	X			
Polyols – Humectants 5%-70%	X	X	X	X	X	X	X	X	X	X
Oil phase 20% - 90%										
Dicaprylyl Ether	X					X		X		

Ingredients	1	2	3	4	5	6	7	8	9	10
Phenyl Trimethicone		X					X			
Hydrogenated Polyisobutene			X							
Isopropyl Isostearate				X					X	
Oleogel basis (Mineral oil and hydrogenated Butylene/Ethylene or Ethylene/Propylene Styrene Copolymer)					X					X
Silicone wax 1%-10%	X	X	X	X	X	X	X	X	X	X
Dimethiconol Behenate	X	X	X	X	X	X	X	X	X	X
Dimethiconol Stearate	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X	X	X	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 0,1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X

Light/dry cosmetic oils

Ingredients	1	2	3	4
Lipophilic base				
Hydrocarbon oils 30%-70%	X			X
Fatty acid esters branched or not 10%-50%		X	X	
Light feel agent				
Silicones/Siloxanes 0% - 10%	X		X	
Perfluorinated oils and Perfluoroethers 0%-10%		X		X
Viscosifying agents 0%-10%	X	X	X	X
Waxes				
Esters of long chain acids and alcohols 0% - 2%	X	X	X	X
Antioxidants 0.1%-1%	X	X	X	X
Solubilizants/dispersing agents 0%-5%	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X
UV-absorber according to the invention 0,1%-20%.	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X

Foaming/mousse products

Ingredients	
SD Alcohol 40 0%-8%	X
Propellant 8%-15%	X
Nonionic Emulsifier/Surfactant 0.5% - 3%	X
Corrosion Inhibitor 0% - 1%	X
Perfume oils 0.1% - 0.5%	X

<b>Ingredients</b>	
Preservatives 0.1%-1%	X
Miscellaneous 0%-1%	X
UV-absorber according to the invention 0,1%-20%.	X
UV-absorber as described in table 1-3 0%-30%	X

#### Stick products

<b>Ingredients</b>	
Waxes 15%-30%	X
Natural and silicone oils 20%-75%	X
Lanoline derivatives 5%->50%	X
Esters of lanolin	x
Acetylated lanolin	x
Lanolin oil	x
Colorants and pigments 10% - 15%	X
Antioxidants 0.1% - 0.8%	X
Perfume oils 0.1% - 2%	X
Preservatives 0.1%-0.7%	X
UV-absorber according to the invention 0,1%-20%	X
UV-absorber as described in table 1-3 0%-30%	X

#### Liquid and compact

<b>Ingredients</b>	<b>1</b>	<b>2</b>
<b>Liquid foundation</b>		
Powder phase 10%-15%	X	
Oil phase 30% - 40%; 75% (only for anhydrous form)	X	
Thickener/suspending agents 1%-5%	X	
Film forming polymers 1%-2%	X	
Antioxidants 0.1% - 1%	X	
Perfume oils 0.1% - 0.5%	X	
Preservatives 0.1%-0.8%	X	
Water deionized Qs 100%	X	
<b>Compact powder</b>		
Powder phase 15%-50%		X
Oil phase 15% - 50%		X
Polyol phase 5% - 15%		X
Antioxidants 0.1%-1%		X
Perfume oils 0.1% - 0.5%		X
Preservatives 0.1%-0.8%		X
<b>For the two product forms</b>		
UV-absorber according to the invention 0,1%-20%	X	X

Ingredients	1	2
UV-absorber as described in table 1-3 0%-30%	X	X

Conditioning Shampoos

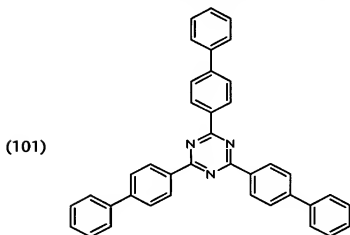
Ingredients	1
Primary surfactants (listed previously) 5%-10%	X
Secondary surfactants (listed previously) 5%-15%	X
Foam Stabilizers (listed previously) 0%-5%	X
Water deionized 40%-70%	X
Actives 0-10%	X
Conditioners	x
Refatting agents	x
Moisturizing agents	x
Thickeners/Rheology modifiers 0%-3%	X
Humectants 0 %-2%	X
PH adjusting agents 0 %-1%	X
Preservatives 0.05 %-1%	X
Perfume oils 0.1%-1%	X
Antioxidants 0.05 %-0.20%	X
Chelating Agents (EDTA) 0%-0.2%	X
Opacifying agents 0%-2%	X
UV-absorber according to the invention 0,1%-20%	X
UV-absorber as described in table 1-3 0%-30%	X

The cosmetic preparation according to the invention is distinguished by excellent protection of human skin against the damaging effect of sunlight.

## Examples

### Preparation of UV absorbers

#### Example 1: Preparation of the compound of formula (101)



Cyanuric chloride (36.9 g, 0.20 mol) is dissolved in 1,2-dichlorobenzene (500 ml). Aluminum chloride (96.0 g, 0.72 mol) is added and the reaction mixture is heated up 140°C. Biphenyl (111.0 g, 0.72 mol), dissolved in 200 ml 1,2-dichlorobenzene, is added slowly dropwise and the temperature is maintained at 140-145°C for 1 to 4 hours).

The reaction mixture is cooled down to about 60°C and added to a mixture of 150ml conc. HCl and 350g ice. After phase separation at about 110°C the dichloro benzene phase is removed, stirred with Na<sub>2</sub>CO<sub>3</sub> and filtered hot at 100 – 110°C. The desired compound recrystallizes from the filtrate.

For purification the compound is recrystallized from dichlorobenzene and dioxane.

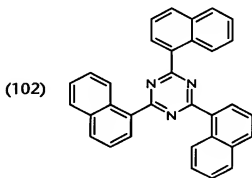
<sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>, TMS):

Peak Nr.	δ (ppm)	%Int.	Peak Nr.	δ (ppm)	%Int.
1	171.8	15.6	6	129.3	98.6
2	145.6	21.6	7	128.4	32.5
3	140.8	18.3	8	127.8	62.9
4	135.6	26.4	9	127.7	100.0



5	129.9	62.2			
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Example 2: Preparation of the compound of formula (102)



According to the procedure described in Example 1 the compound of formula (102) is obtained, if naphthalene is used instead of biphenyl.

Example 3. Preparation of micronized UV absorbers

100 parts of the compound of formula (101) are milled together with zirconium silicate bells (diameter: 0,1 to 4 mm) as grinding aids, a dispersing agent (15 parts of  $C_8-C_{16}$  polyglucoside) and water (85 parts) in a ball mill to a mean particle size of  $d_{50} = 200\text{nm}$ . With this method a micropigment dispersion of a UV absorber is obtained.

Example 4:

100 parts of the compound of formula (101) are milled together with zirconium silicate bells (diameter: 0,1 to 4 mm) as grinding aids, a dispersing agent (15 parts  $C_{12}$  glyceride-PEG10) and water (85 parts) in a ball mill to a mean particle size of  $d_{50} = 200\text{nm}$ . With this method a micropigment dispersion of a UV absorber is obtained.

## Application Examples

### Example 5: UV-A/UV-B Daily Care UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Oleth-3 Phosphate	0.60
	Steareth-21	2.50
	Steareth-2	1.00
	Cetyl Alcohol	0.80
	Stearyl Alcohol	1.50
	Tribehenin	0.80
	Isohexadecane	8.00
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	2.00
	UV-absorber dispersion as described in example 3	3.00
	Disodium EDTA	0.10
Part C	Water	20.00
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and)	1.50
	PPG-1 Trideceth-6	
	Cyclopentasiloxane	4.50
	PEG-12 Dimethicone	2.00
	Tocopheryl Acetate	0.45
	Water (and) Citric Acid	qs
Part E	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part A is poured into part B under continuous stirring. Immediately after the emulsification, Cyclopentasiloxane and PEG-12 Dimethicone from part D are incorporated into the mixture. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000 rpm for 30 sec. After cooling down to 65°C Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6 are incorporated. Part C is added at a temperature < 50°C. At a temperature ≤ 35°C Tocopheryl Acetate is incorporated and subsequently the pH is adjusted with Water (and) Citric Acid. At room temperature part E is added.

Example 6: UV Day Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Cetyl Phosphate	1.75
	C12-C15 Alkyl Benzoate	5.00
	Cetearyl Alcohol/ PEG-20 Stearate	2.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.50
	Ethylhexyl Methoxycinnamate	3.00
	Isononyl Isononanoate	2.00
Part B	Aqua	qs to 100
	Xanthan Gum	0.35
	UV-absorber dispersion as described in example 3	5.00
	Disodium EDTA	0.20
	Propylene Glycol	2.00
	Diazolidinyl Urea (and) Methylparaben (and) Propylparaben (and)	0.70
	Propylene Glycol Glycerin	1.50
Part C	Cyclopentasiloxane (and) Dimethiconol	1.00
	Ethoxydiglycol	3.00
	Dimethicone	2.00

<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part D Triethanolamine	qs

Manufacturing instruction:

Part A by is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part B s prepared and heated to 75°C. At this temperature part B is poured into part A under progressive stirring speed. Then the mixture is homogenized (30sec., 15000 rpm) . At a temperature < 55°C the ingredients of part C are incorporated. The mixture is cooled down under moderate stirring, then the pH is checked and adjusted with triethanolamine.

Example 7: Sun Protection Emulsion

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.00
	C12-15 Alkyl Benzoate	2.00
	Dicaprylyl Ether	3.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.00
	Ethylhexyl Methoxycinnamate	3.00
	Sodium Acrylates Copolymer (and) Glycine Soja (and) PPG-1 Trideceth-6	0.30
	Squalane	3.50
Part B	Aqua	qs to 100
	UV-absorber dispersion as described in example 3	5.00
Part C	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	2.50
	Aqua	10.00
Part D	Cyclopentasiloxane, Dimethiconol	2.00
	Ethoxydiglycol	5.00

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
	Cyclopentasiloxane (and) Dimethicone/Vinyl-dimethicone Crosspolymer	2.00
Part E	Sodium Hydroxide	0.10

Manufacturing instruction:

Part A is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part B is prepared and heated to 75°C. At this temperature, part B is poured into part A under progressive stirring speed. Below 65°C the ingredients of part D are added separately. After cooling down under moderate stirring to 55°C part C is added. The pH is then checked and adjusted with sodium hydroxide. The mixture is homogenized for 30 sec at 16000rpm.

Example 8: Every Day Lotion

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Stearyl Phosphate	5.00
	Tricontanyl PVP	1.00
	Ethoxydiglycol Oleate	3.00
	Squalane	5.00
	C12-15 Alkyl Benzoate	5.00
	Ethylhexyl Methoxycinnamate	3.00
	Glyceryl Stearate	2.00
	Cetyl Alcohol	2.00
Part B	Aqua	20.00
	UV-absorber dispersion as described in example 3	3.00
Part C	Aqua	qs to 100
	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
	Glycerin	2.50
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15

<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Sodium Lauroyl Glutamate	0.70
Part D Cyclopentasiloxane (and) Dimethiconol	1.50
Triethanolamine	1.85

Manufacturing instruction:

Part A is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part C is prepared and heated to 75°C. Part C is poured into the part A under moderate stirring. Immediately after the emulsification part B is added, then neutralized with a part of the triethanolamine. The mixture is homogenized for 30 sec. After cooling down under moderate stirring Cyclopentasiloxane (and) Dimethiconol are added. Below 35°C the pH is checked and adjusted with triethanolamine.

Example 9: Sprayable Sunscreen Emulsion

<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A Cetareth-15 (and) Glyceryl Stearate	3.00
Stearyl Alcohol	1.00
Cetyl Ricinoleate	0.80
Dicaprylyl Ether	3.00
C12-15 Alkyl Benzoate	3.00
Isohexadecane	2.50
Stearyl Dimethicone	1.00
Ethylhexyl Methoxycinnamate	4.00
Cetyl Alcohol	0.80
Di-C12-13 Alkyl Tartrate	3.00
Part B Aqua	qs to 100
Steareth-10 Allyl Ether/Acrylates Copolymer	0.45
PEG-7 Glyceryl Cocoate	2.50
Glycerin	2.00
Propylene Glycol	3.00

<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part C Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
Aqua	20.00
UV-absorber dispersion as described in example 3	12.00
Titanium Dioxide (and) Silica (and) Sodium Polyacrylate	8.00
Part D Cyclopentasiloxane (and) Dimethiconol	0.85
Part E Sodium Hydroxide (and) Water	qs to pH 6.50
Part F Fragrance	-7.00
	qs

#### Manufacturing instruction

Part A and part B are heated up to 80°C. Part A is blended into part B under stirring and homogenized with an UltraTurrax at 11 000 rpm for 30 sec. Part C is heated to 60°C and added slowly to the emulsion. After cooling down to 40°C part D is incorporated at room temperature and part E is added.

#### Example 10: Daily Care Lotion

<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A Polyglyceryl Methyl Glucose Distearate	2.50
Cetearyl Alcohol	2.00
Octyl Stearate	3.00
Caprylic/Capric Triglyceride	4.00
Isohexadecane	4.00
Ethylhexyl Methoxycinnamate	2.70
Part B Aqua	64.80
Glycerin	5.00
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and)	0.50
Ethylparaben (and) Propylparaben	
UV-absorber dispersion as described in example 3	8.00

<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part C Cyclomethicone (and) Dimethicone	3.00
Part D Steareth-10 Allyl Ether/Acrylates Copolymer	0.50

Manufacturing instruction

Part A and B are heated to 75°C. Part A is added into part B under continuous stirring and homogenized with 11000 rpm for 1 minute. After cooling down to 50°C part C is added under continuous stirring. After cooling further down to 30°C part D is added. Afterwards the pH is adjusted between 6.00 - 6.50.

Example 11: Daily Care with UV Protection

<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A Glyceryl Stearate SE	3.00
Glyceryl Stearate and PEG-100 Stearate	3.50
Cetyl Alcohol	1.50
Myristyl Myristate	2.00
Isopropyl Palmitate	2.50
Paraffinum Perliquidum	5.00
Octyl Dimethyl PABA	3.00
Part B Aqua	qs to 100
Propylene Glycol	7.50
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	1.00
Part C Aqua	30.00
UV-absorber dispersion as described in example 3	10.00
Part D Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	2.00
Part E Citric Acid	0.30



Manufacturing instruction:

Part A and B are heated separately to 75°C. After adding part B into part A the mixture is homogenized with Ultra Turrax for one minute at 11000 rpm. After cooling down to 50°C part C is added. Afterwards the mixture is homogenized for one minute at 16000 rpm. At a temperature < 40°C part D is added. At room temperature the pH-value is adjusted with part E between 6.00 and 6.50.

Example 12: O/W Every Day UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	C12-15 Alkyl Benzoate	5.00
	Isopropyl Palmitate	5.00
	Ethylhexyl Methoxycinnamate	3.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 3	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.

Example 13: O/W Every Day UV Protection

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	C12-15 Alkyl Benzoate	5.00
	Isopropyl Palmitate	5.00
	Ethylhexyl Methoxycinnamate	3.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 3	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.

Example 14: Sunscreen Cream

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.50
	C12-15 Alkyl Benzoate	6.00
	Caprylic/Capric Triglyceride	7.00
	Pentaerythritol Tetraisostearate	2.00
	Ethylhexyl Methoxycinnamate	3.00
	Isoamyl p-Methoxycinnamate	2.00
Part B	Aqua	qs to 100
	Glycerin	2.00
	Propylene Glycol	1.50
	Magnesium Aluminium Silicate	1.20
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
	UV-absorber dispersion as described in example 3	12.00
Part D	Phenyl Trimethicone	1.50
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.70
Part E	Sodium Hydroxide	0.90

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part B is added into part A under continuous stirring and afterwards homogenized with Ultra Turrax for 30sec at 11000 rpm . After

cooling down to 60°C part C is added. At 40°C part C is added and homogenized for 15sec at 11000 rpm. At room temperature the pH-value is adjusted with part E.

Example 15: UVA/UVB Daily Care Lotion, type O/W

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Mineral Oil	15.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 3	8.00
Part D	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and)	0.70
	Butylparaben (and) Propylparaben (and) Isobutylparaben	
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately to 75°C; part C to 60°C. Part B is poured into part A under stirring. After one-minute of homogenization at 11000 rpm part C is added to the mixture of A/B. After cooling down to 40°C part D is incorporated. At room temperature the pH value is adjusted with part E between 6.3 and 7.0. Finally part F is added.

Example 16: UVA/UVB Daily Care Lotion, type O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Oleth-3 Phosphate	0.60
	Steareth-21	2.50
	Steareth-2	1.00
	Cetyl Alcohol	0.80
	Stearyl Alcohol	1.50
	Tribehenin	0.80
	Isohexadecane	8.00
Part B	Water	qs to 100
	Glycerin	2.00
	Disodium EDTA	0.10
Part C	Cyclopentasiloxane	4.50
	PEG-12 Dimethicone	2.00
Part D	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1	1.50
	Trideceth-6	
Part E	UV-absorber dispersion as described in example 3	10.00
Part F	Tocopheryl Acetate	0.45
	DMDM Hydantoin (and) Iodopropynyl Butylcarbamate (and)	0.85
	Aqua (and) Butylene Glycol	
Part G	Water (and) Citric Acid	qs
	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part A is poured into part B under stirring. Immediately after the emulsification, part C is added to the mixture and homogenized with an Ultra Turrax at 11000 rpm for 30 sec. After cooling down to 65°C Sodium Acrylates

Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6 At 50°C is added slowly to the UV absorber dispersion. At about 35-30°C part F is incorporated. The pH is adjusted with part G between 5.5 and 6.5.

Example 17: UV-A/UV-B Every Day Protection Lotion O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Glyceryl Dilaurate	2.00
	Ethylhexyl Palmitate	6.00
	Cetyl Alcohol	1.00
	Glyceryl Stearate	2.00
	Laureth-23	1.00
	Isopropyl Palmitate	2.00
	Tribehenin	0.80
	Beeswax	1.50
	Lanolin Oil	1.00
Part B	Water	qs to 100
	Propylene Glycol	4.00
	Water (and) Titanium Dioxide (and) Alumina (and) Sodium Metaphosphate (and) Phenoxyethanol (and) Sodium Methylparaben	4.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	1.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
	UV-absorber dispersion as described in example 3	8.00
Part E	Water (and) Sodium Hydroxide	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part A is poured into part B while stirring and homogenized with an Ultra Turrax by 11000 rpm for 30 sec. After cooling down to 60°C part C is incorporated. At 40°C part D is added slowly under continuous stirring. The pH is adjusted with part E between 6.50 - 7.00.

Example 18: Sprayable Sunscreen Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Potassium Cetyl Phosphate	0.20
	Isohexadecane	7.00
	VP/Eicosene Copolymer	1.50
	Di-C12-13 Alkyl Tartrate	6.00
	Ethylhexyl Triazone	2.50
	C12-15 Alkyl Benzoate	4.50
Part B	Water	qs to 100
	Sorbeth-30	2.00
	Sorbitan Stearate (and) Sucrose Cocoate	4.00
	Titanium Dioxide (and) Alumina (and) Silica (and) Sodium Polyacrylate	2.50
Part C	Water	30.00
	UV-absorber dispersion as described in example 3	12.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
Part E	Water (and) Citric Acid	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C, part C is heated to 50°C. Part B is poured into part A and homogenized with an Ultra Turrax for 1 minute at 11000 rpm. After cooling down to 50°C part C is added under continuous stirring. At 40°C part D is incorporated and homogenized again for 10 sec. at 11000 rpm. The pH is adjusted with part E.

**Example 19: O/W Every Day UV Protection Lotion**

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	Caprylic/Capric Triglyceride	5.00
	Isopropyl Palmitate	5.00
	Ethylhexyl Methoxycinnamate	3.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 3	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and)	0.70
	Butylparaben (and) Propylparaben (and) Isobutylparaben	
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

**Manufacturing instruction:**

Part A and part B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.



Example 20: Water resistant Sunscreen Emulsion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Polyglyceryl-10 Pentastearate (and) Behenyl Alcohol (and) Sodium Stearoyl Lactylate	2.50
	VP/Eicosene Copolymer	1.50
	Stearyl Alcohol	1.50
	Squalane	4.00
	C12-15 Alkyl Benzoate	7.50
	Octocrylene	1.50
	4-Methylbenzylidene Camphor	3.00
	Ethylhexyl Methoxycinnamate	2.00
Part B	Water	qs to 100
	Glycerin	1.80
	Steareth-10 Allyl Ether/Acrylates Copolymer	0.80
Part C	UV-absorber dispersion as described in example 3	9.00
Part D	VP/Hexadecene Copolymer	2.70
	Cyclomethicone	1.50
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
Part E	Aqua (and) Tocopheryl Acetate (and) Caprylic/Capric Triglyceride (and) Polysorbate 80 (and) Lecithin	3.50
Part F	Fragrance	qs
	Water (and) Sodium Hydroxide	qs

Manufacturing instruction:

Part A and part B are heated separately to 80°C. Part A is poured into part B under continuous stirring. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000 rpm for 1 min. After cooling down to 60°C part C is incorporated. At 40°C part D is added and the mixture homogenized for a short time again. At 35°C part E is added and at room temperature Fragrance is added. Finally the pH is adjusted with Sodium Hydroxide.

Example 21: UVA/UVB Sun Protection Lotion, O/W type

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Potassium Cetyl Phosphate	2.00
	Tricontanyl PVP	1.00
	Caprylic/Capric Triglyceride	5.00
	C12-15 Alkyl Benzoate	5.00
	Cetearyl Isononanoate	5.00
	Glyceryl Stearate	3.00
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	3.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
Part D	UV-absorber dispersion as described in example 3	8.00
Part E	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
Part F	Water (and) Sodium Hydroxide	qs to pH 7.00
Part G	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part B is poured into part A under moderate stirring. The mixture is homogenized with an Ultra Turrax at 11000 rpm for 1 minute. After cooling down to 70°C part C is added under stirring. After cooling further down to 50°C part D is incorporated very slowly. At 40°C part E is added. At room temperature the pH adjusted with part F to 7.00 and part G is added.

Example 22: UVA/UVB Sun Protection Lotion, O/W type

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Potassium Cetyl Phosphate	2.00
	Tricontanyl PVP	1.00
	Caprylic/Capric Triglyceride	5.00
	C12-15 Alkyl Benzoate	5.00
	Cetearyl Isononanoate	5.00
	Glyceryl Stearate	3.00
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	3.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
Part D	UV-absorber dispersion as described in example 3	20.00
Part E	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
Part F	Water (and) Sodium Hydroxide	qs to pH 7.00
Part G	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part B is poured into part A under moderate stirring. The mixture is homogenized with an Ultra Turrax at 11000 rpm for 1 minute. After cooling down to 70°C add part C is added under stirring. After cooling further down to 50°C part D is incorporated very slowly. At 40°C part E is added. At room temperature the pH is adjusted with part F to 7.00 and part G is added.

**Example 23: Sunscreen Lotion**

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.00
	C12-15 Alkyl Benzoate	2.00
	Dicaprylyl Ether	3.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.00
	Ethylhexyl Methoxycinnamate	3.00
	Sodium Acrylates Copolymer (and) Glycine Soja (and) PPG-1 Trideceth-6	0.30
	Squalane	3.50
	VP/Eicosene Copolymer	2.00
Part B	Water	qs to 100
	UV-absorber dispersion as described in example 3	5.00
Part C	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	2.50
	Water	10.00
Part D	Cyclopentasiloxane (and) Dimethiconol	2.00
	Ethoxydiglycol	5.00
	Cyclopentasiloxane (and) Dimethicone/Vinyl Dimethicone Crosspolymer	2.00
Part E	Aqua (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction

Part A and part B are heated separately up to 75°C. Part B is poured into part A under progressive stirring speed. At a temperature < 65°C the ingredients of part D are added separately. After cooling down to 55°C under moderate stirring part C is added. At a temperature < 35°C the pH is checked and adjusted with Sodium Hydroxide and homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm. At room temperature part F is added.

Example 24: W/O Sunscreen Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	PEG-7 Hydrogenated Castor Oil	3.00
	Polyglyceryl-3 Diisostearate	4.00
	Microcrystalline Wax	1.00
	Magnesium Stearate	1.50
	Propylparaben	0.10
	Mineral Oil	15.00
	Octyldodecanol	8.00
	Ethylhexyl Triazone	1.00
	Ethylhexyl Methoxycinnamate	2.00
Part B	Water	qs to 100
	Water (and) Citric Acid	0.05
	Methylparaben	0.15
	Magnesium Sulfate	0.50
Part C	UV-absorber dispersion as described in example 3	9.00
	Fragrance	qs

Manufacturing instruction:

Part A is heated to 80°C whilst stirring. Part B is added into part A and homogenized with an Ultra Turrax at 11 000 rpm for one minute. After cooling down to 30°C part C is incorporated.

Example 25: Skin Protection Sunscreen Lotion W/O

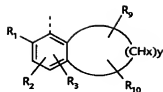
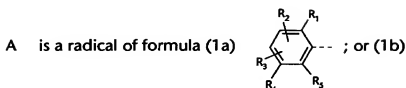
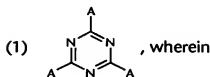
	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Polyglyceryl-2 Dipolyhydroxystearate	3.00
	Glyceryl Oleate	3.00
	Cetearyl Isononanoate	7.00
	Hexyl Laurate	6.00
	Dicaprylyl Ether	6.00
	Propylparaben	0.10
	Hexyldecanol	3.00
	Magnesium Stearate	1.00
	Beeswax	1.00
	Ethylhexyl Methoxycinnamate	4.00
Part B	Water	qs to 100
	Methylparaben	0.15
	Magnesium Sulfate	1.00
Part C	UV-absorber dispersion as described in example 3	6.00

Manufacturing instruction:

Part A is heated separately to 80°C under gentle stirring. Part B is added to part A and homogenized for one minute at 11000 rpm. After cooling down to 30°C part C is added under continuous stirring.

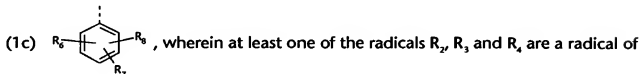
Claims:

1. Use of the compounds of formula



R<sub>1</sub> and R<sub>5</sub> independently from each other are hydrogen; C<sub>1</sub>-C<sub>18</sub>alkyl; or C<sub>6</sub>-C<sub>12</sub>aryl;

R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently from each other are hydrogen; or a radical of formula



formula (1c);

R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> independently from each other are hydrogen; hydroxy; halogen; C<sub>1</sub>-C<sub>18</sub>alkyl; C<sub>1</sub>-C<sub>18</sub>alkoxy; C<sub>6</sub>-C<sub>12</sub>aryl; C<sub>6</sub>-C<sub>12</sub>aryloxy; C<sub>1</sub>-C<sub>18</sub>alkylthio; carboxy; -COOM; C<sub>1</sub>-C<sub>18</sub>alkylcarboxyl; aminocarbonyl; or mono- or di-C<sub>1</sub>-C<sub>18</sub>alkylamino; C<sub>1</sub>-C<sub>10</sub>acylamino; -COOH;

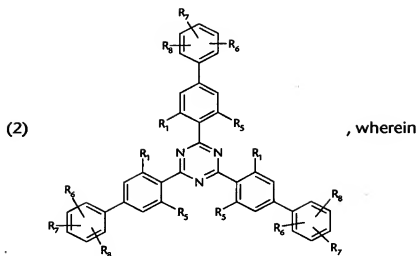
M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

2. Use according to claim 1, which relates to compounds of formula



$R_1$ ,  $R_3$ ,  $R_6$ ,  $R_7$ , and  $R_8$  are defined as in claim 1.

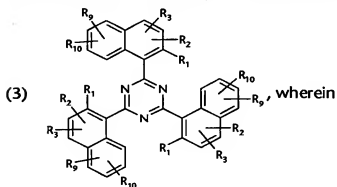
3. Use according to claim 1 or 2, wherein  $R_1$  and  $R_3$  are hydrogen.

4. Use according to one of claims 1 to 3, wherein  $R_6$  and  $R_8$  are hydrogen.

5. Use according to one of claims 1 to 4, wherein

$R_1$  is hydrogen; hydroxy;  $C_1$ - $C_3$ alkyl;  $C_1$ - $C_3$ alkoxy;  $-COOM$ ;  $-COOH$ ; or  $COOR_{10}$ ; and  $R_{10}$  is  $C_1$ - $C_3$ alkyl.

6. Use according to claim 1, which relates to compounds of formula



$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_9$ , and  $R_{10}$  are defined as in claim 1.

7. Use according to claim 6, wherein

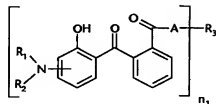
$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_9$ , and  $R_{10}$  are hydrogen; or  $C_1$ - $C_{18}$ alkyl.



7. A cosmetic preparation comprising at least one or more compounds of formula (1) according to claim 1 together with cosmetically tolerable carriers or adjuvants.

8. Cosmetic preparation according to claim 7 comprising the UV filter combination (A) (a<sub>1</sub>) at least one symmetrical triazine derivative of formula (1) and

(a<sub>2</sub>) at least one aminobenzophenone derivative of formula



wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are; C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>3</sub>-C<sub>10</sub>cycloalkyl; C<sub>3</sub>-C<sub>10</sub>cycloalkenyl; or R<sub>1</sub> and R<sub>2</sub> together with the linking nitrogen atom form a 5- or 6-membered heterocyclic ring;

n<sub>1</sub> is a number from 1 to 4;

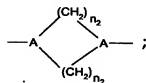
when n<sub>1</sub> = 1,

R<sub>3</sub> is a saturated or unsaturated heterocyclic radical; hydroxy-C<sub>1</sub>-C<sub>3</sub>alkyl; cyclohexyl optionally substituted with one or more C<sub>1</sub>-C<sub>3</sub>alkyl; phenyl optionally substituted with a heterocyclic radical, aminocarbonyl or C<sub>1</sub>-C<sub>3</sub>alkylcarboxy;

when n<sub>1</sub> is 2,

R<sub>3</sub> is an alkylene-, cycloalkylene, alkenylene or phenylene radical which is optionally substituted by a carbonyl- or carboxy group; a radical of formula  $\text{---CH}_2\text{---C}\equiv\text{C---CH}_2\text{---}$  or R<sub>3</sub>

together with A forms a bivalent radical of the formula (1a)



wherein

n<sub>2</sub> is a number from 1 to 3;

when n<sub>1</sub> is 3,

R<sub>3</sub> is an alkanetriyl radical;

wenn n<sub>1</sub> is 4,

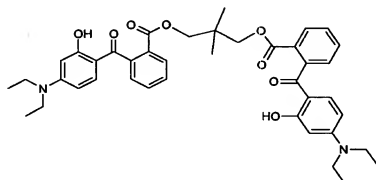
R<sub>3</sub> is an alkanetetrayl radical;

A is -O-; or -N(R<sub>4</sub>)-; and

R<sub>4</sub> is hydrogen; C<sub>1</sub>-C<sub>3</sub>alkyl; or hydroxy-C<sub>1</sub>-C<sub>3</sub>alkyl.

9. Cosmetic preparation according to claim 8 comprising the UV filter combination (A1)

(a.) the compound of formula (6); and

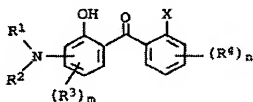


(a.) the compound of formula

10. Cosmetic preparation according to claim 7 comprising the UV filter combination (B)

(b.) at least one symmetrical triazine derivative of formula (1); and

(b.) at least one aminobenzophenone derivative of the formula



wherein

$R^1$ ,  $R^2$  independently from each other is hydrogen,  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_3$ - $C_{10}$ cycloalkenyl; wherein  $R^1$  and  $R^2$  may form a five- or six-membered ring;

$R^3$ ,  $R^4$  independently from each other is  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_3$ - $C_{10}$ cycloalkenyl,  $C_1$ - $C_{20}$ alkoxy,  $C_1$ - $C_{20}$ alkoxycarbonyl,  $C_1$ - $C_{20}$ alkylamino, di( $C_1$ - $C_{20}$ alkyl)amino, optionally substituted aryl or heteroaryl;

X is hydrogen;  $COOR^5$ ;  $CONR^6R^7$ ;

$R^5$ ,  $R^6$ ,  $R^7$  independently from each other is hydrogen,  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_3$ - $C_{10}$ cycloalkenyl;  $C_3$ - $C_{10}$ cycloalkenyl;  $(Y-O)_n$ -Z; optionally substituted Aryl;

Y is  $-(CH_2)_2$ -;  $-(CH_2)_3$ -;  $-(CH_2)_4$ -;  $-CH(CH_3)-CH_2$ -;

Z is  $-CH_2-CH_3$ ;  $-CH_2-CH_2-CH_3$ ;  $-CH_2-CH_2-CH_2-CH_3$ ;  $CH(CH_3)-CH_3$ ;

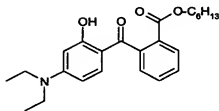
m is 0; 1; 2; or 3;

n is 0; 1; 2; 3; or 4; and

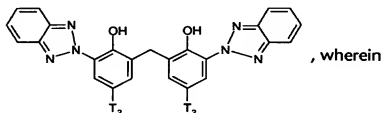
q is a number from 1 to 20.

11. Cosmetic preparation according to claim 10 comprising the UV filter combination (B1)  
(b<sub>1</sub>) the compound of formula (6) and

(b<sub>2</sub>) the compound of formula



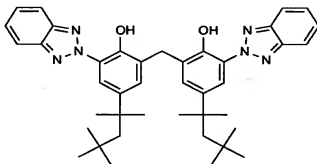
12. Cosmetic preparation according to claim 7 comprising the UV filter combination (C)  
(c<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and  
(c<sub>2</sub>) at least one benzotriazole derivative of formula



$T_2$  is  $C_1$ - $C_{10}$  alkyl, or phenyl-substituted  $C_1$ - $C_4$  alkyl.

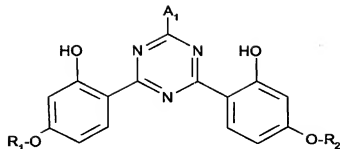
13. Cosmetic preparation according to claim 12 comprising the UV filter combination (C1)  
(c<sub>1</sub>) the compound of formula (6) and

(c<sub>2</sub>) the compound of formula



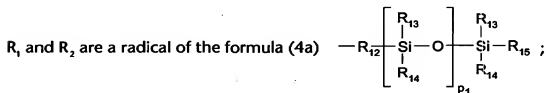
14. Cosmetic preparation according to claim 7 comprising the UV filter combination (D)  
(d<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and

(d<sub>2</sub>) at least one compound of formula



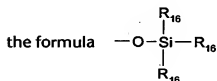
in which

R<sub>1</sub> and R<sub>2</sub>, independently of one another, are C<sub>3</sub>-C<sub>18</sub>alkyl; C<sub>2</sub>-C<sub>16</sub>alkenyl; a radical of the formula -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-T<sub>1</sub> ; or



R<sub>12</sub> is a direct bond; a straight-chain or branched C<sub>1</sub>-C<sub>8</sub>alkylene radical or a radical of the formula -C<sub>m1</sub>H<sub>2m1</sub>- or -C<sub>m1</sub>H<sub>2m1</sub>-O- ;

R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub>, independently of one another, are C<sub>1</sub>-C<sub>18</sub>alkyl; C<sub>1</sub>-C<sub>18</sub>alkoxy or a radical of

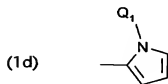


R<sub>16</sub> is C<sub>1</sub>-C<sub>3</sub>alkyl;

m<sub>1</sub> and m<sub>2</sub>, independently of one another, are 1 to 4;

p<sub>1</sub> is 0 or a number from 1 to 5;

A<sub>1</sub> is a radical of the formula



$R_3$  is hydrogen;  $C_1$ - $C_{10}$ alkyl,  $-(CH_2CHR_5-O)_{n_1}-R_4$  ; or a radical of the formula

$-CH_2-CH(-OH)-CH_2-O-T_1$ ;

$R_4$  is hydrogen; M;  $C_1$ - $C_3$ alkyl; or a radical of the formula  $-(CH_2)_{m_2}-O-T_1$  ;

$R_5$  is hydrogen; or methyl;

$T_1$  is hydrogen; or  $C_1$ - $C_8$ alkyl;

$Q_1$   $C_1$ - $C_{18}$ alkyl;

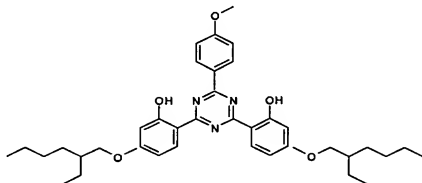
M is a metal cation;

$m_2$  is 1 to 4; and

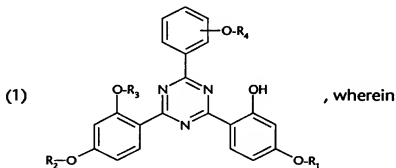
$n_1$  is 1-16.

15. Cosmetic preparation according to claim 14 comprising the UV filter combination (D1)  
(d.) the compound of formula (6) and

(d.) the compound of formula



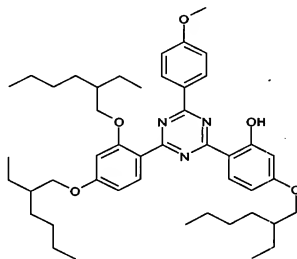
16. Cosmetic preparation according to claim 7 comprising the UV filter combination (E)  
(e.) at least one symmetrical triazine derivative of formula (1) and  
(e.) at least one hydroxyphenyltriazine compound of formula



R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>18</sub>alkyl; C<sub>2</sub>-C<sub>10</sub>alkenyl; or phenyl-  
C<sub>1</sub>-C<sub>8</sub>alkyl;

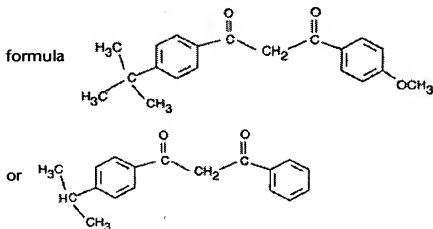
R<sub>4</sub> is hydrogen; or C<sub>1</sub>-C<sub>8</sub>alkyl.

17. Cosmetic preparation according to claim 16 comprising the UV filter combination (E1)  
(d.) the compound of formula (6) and



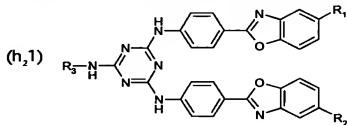
- (d.) the compound of formula

18. Cosmetic preparation according to claim 7 comprising the UV filter combination (F)  
(f.) at least one symmetrical triazine derivative of formula (1); and  
(f.) at least one dibenzoylmethane derivative of



19. Cosmetic preparation according to claim 7 comprising the UV filter combination (G)  
(g.) at least one symmetrical triazine derivative of formula (1); and  
(g.) disodium phenyl dibenzimidazole tetrasulfonate.

20. Cosmetic preparation according to claim 7 comprising the UV filter combination (H)  
 (h<sub>1</sub>) at least one symmetrical triazine derivative of formula (1); and  
 (h<sub>2</sub>) at least one benzoxazole-substituted triazine of the formula



wherein

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently from each other are branched or unbranched C<sub>1</sub>-C<sub>12</sub>alkyl.

21. Cosmetic preparation according to claim 20 comprising the UV filter combination (H1)  
 (h<sub>1</sub>) the compound of formula (6) and  
 (h<sub>2</sub>) at least one of the compound of formula (h<sub>2</sub>1), wherein  
 R<sub>1</sub> and R<sub>2</sub> independently from each other are tert. butyl; or tert. amyl; and  
 R<sub>3</sub> is tert.butyl, tert.octyl; or 2-ethylhexyl.

22. Cosmetic preparation according to claim 20 or 21 comprising the UV filter combination (H2)

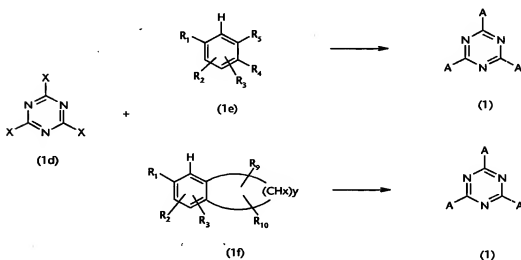
- (h<sub>2</sub>) the compound of formula (6) and  
 (h<sub>2</sub>) at least one of the compound of formula (h<sub>2</sub>1), wherein  
 (h<sub>2a</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.amyl; and R<sub>3</sub> is tert.butyl; or wherein  
 (h<sub>2b</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.butyl and R<sub>3</sub> is tert.octyl; or wherein  
 (h<sub>2c</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.butyl; and R<sub>3</sub> is 2-ethylhexyl; or wherein  
 (h<sub>2d</sub>) R<sub>1</sub> and R<sub>2</sub> are tert.amyl; and R<sub>3</sub> is 2-ethylhexyl.

23. Cosmetic preparation according to claim 7 comprising the UV filter combination (I)  
 (i<sub>1</sub>) a symmetrical triazine derivatives of formula (1); and  
 (i<sub>2</sub>) 2-(2H-benzotriazol-2-yl)-4-methyl-6-[1,3,3,3-tetramethyl-1-  
 [(trimethylsilyl)oxy]disiloxanyl]propyl]-.

24. Cosmetic preparation according to claim 7 comprising the UV filter combination (K)  
 (k<sub>1</sub>) symmetrical triazine derivatives of formula (1) and

(k<sub>2</sub>) siloxanes and silicones, di-Me, 1-[[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]phenoxy]methyl]ethenyl Me, 3-[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]phenoxy]-1-propenyl Me, Me hydrogen

25. A process for the preparation of the compound of formula (1), comprising reacting a halogen triazine compound of formula (1d) in a Friedel-Crafts-reaction with an optionally substituted aromatic hydrocarbon of formula (1e) or (1f) to the compound of formula (1) according to the following reaction scheme:



wherein

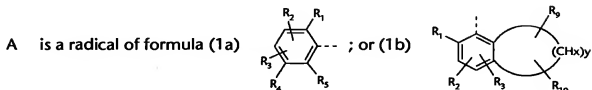
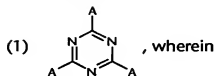
X is fluoro; chloro; oder bromo; and

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>9</sub>, R<sub>10</sub>, x and y are defined as in claim 1.

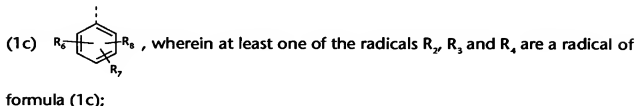


# Abstract

Disclosed is the no-therapeutical use of the compounds of formula



$R_1$  and  $R_3$  independently from each other are hydrogen;  $C_1$ - $C_{18}$ alkyl; or  $C_6$ - $C_{12}$ aryl;  
 $R_2$ ,  $R_3$  and  $R_4$  independently from each other are hydrogen; or a radical of formula



$R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  and  $R_{10}$  independently from each other are hydrogen; hydroxy;  $C_1$ - $C_{18}$ alkyl;  $C_1$ - $C_{18}$ alkoxy;  $C_6$ - $C_{12}$ aryl;  $C_6$ - $C_{12}$ aryloxy;  $C_1$ - $C_{18}$ alkylthio; carboxy;  $-COOM$ ;  $C_1$ - $C_{18}$ -alkylcarboxyl; aminocarbonyl; or mono- or di- $C_1$ - $C_{18}$ alkylamino;

M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

The compounds of formula (1) are high effective UV absorbers for cosmetic formulations and can be – depending on their physical properties be used in micronized or soluble form.